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ANALYTICAL METHODS DEVELOPMENT AND CHARACTERIZATION REQUIREMENTS FOR PROJECTS ON RESOURCE CHARACTERIZATION

FINAL REPORT

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SUMMARY

The objectives of this study were two-fold. The first was to determine which chemical analyses provide the best information to describe the changes occurring in heavy oil as a result of the recovery process. The second was to interpret these changes based on the most appropriate analyses. In order to accomplish these objectives five samples of produced oil from the Cummings formation of the Murphy Eyehill Field of Saskatchewan were characterized by a variety of analytical methods. The measured properties of two primary production samples collected approximately 1 1/2 years apart were compared to those observed for samples produced under fireflood conditions from two different wells.

The density, viscosity and distillation data provided the most rapid and sensitive indication of changes in the quality of the oil. The fireflood produced samples showed marked reduction in viscosity and density as compared to the oil produced under primary conditions. The major change observed in the distillation data was an almost tenfold increase in the naphtha boiling range cut of the fireflood produced oil from one of the wells. More detailed understanding of the changes required fractionation of the distillation cuts by column chromatography with subsequent gas chromatography - mass spectrometry (GC/MS) to provide information on specific compound types. In particular the naphtha and middle distillate cuts both showed increases in lower boiling paraffinic, naphthenic and aromatic compounds. The gas oil and residue portion of the produced oils showed little or no difference between fireflood and primary production. The column chromatographic separations required to simplify the GC/MS analyses were more difficult to reproduce and hence more difficult to use in interpretation of the changes. Elemental analyses and acid number determinations can often be useful for monitoring changes in the oil as a result of combustion. In this study no increase in oxygen content or acid number was observed for the fireflood produced oils, suggesting that the oil was produced relatively far from the firefront. Furthermore, there were no significant changes in sulfur or nitrogen content. Proton (^{1}H) and carbon-13 (^{13}C) nuclear magnetic resonance (NMR) indicated few changes in the aromaticities which could be attributed to changes in specific fractions of the oil.

Overall, the observed changes between primary and fireflood oils suggest that lower boiling materials formed at the firefront by thermal cracking are pushed ahead of the front by combustion gases and steam. These materials probably condensed and dissolved in the oil resulting in lower viscosity and density and higher naphtha content. Some evidence for fractionation of the oil in the reservoir during production was observed. Both the primary and fireflood produced oils showed an increase in density and viscosity in the samples taken 1 1/2 years later.

The changes observed in this study suggest that alteration of the oil due to the fireflood operation would not appreciably affect the refining process. The study should be extended over a larger time period to determine what changes are observed when the firefront approaches the production well.

RESUME

Cette étude avait deux objectifs: la détermination des analyses chimiques qui donneront plus de renseignements pour décrire les changements dans la composition des huiles lourdes qui résultent du procédé de récupération et l'interprétation de ces changements sur la base des analyses les plus appropriées. Pour atteindre ces objectifs, cinq échantillons d'huile produites de la formation Cummings du champ Murphy Eyehill en Saskatchewan furent caracterisées par une variété de méthodes analytiques. Les propriétés mesurées de deux échantillons de récupération primaire recueillis à 18 mois d'intervalle furent comparées à celles observées pour des échantillons produits par combustion in situ dans deux puits différents.

Les plus rapides et les plus sensibles indications des changements survenus dans la qualité de l'huile proviennent de la densité, la viscosité, et des données de distillation. Les échantillons produits par combustion ont démontré une diminution marquée de leurs viscosité et densité comparé aux échantillons d'huile de récupération primaire. Le plus important changement observé dans les données de distillation était une multiplication par dix de la fraction de limite d'ébullition du naphta de l'huile produite par combustion provenant d'un des puits. Une compréhension plus approfondie des changements demande un fractionnement des coupes de distillation par chromatographie sur colonne suivi de chromatographie en phase gazeuse et spectrométrie de masse (CG/SM). En particulier, les fractions naphta et distillat moyen ont toutes deux montré une augmentation des composés paraffiniques, naphténiques et aromatiques à bas point d'ébullition. Les parties gas-oil et residu ont montré peu ou pas de difference quant à l'origine de l'huile produite (primaire ou combustion). Les séparations chromatographiques sur colonne nécessaires pour la simplification des analyses CG/SM furent plus difficiles à reproduire et à interpréter [quant aux changements]. Les analyses des éléments et les déterminations d'indice d'acidité peuvent souvent être utiles pour surveiller les changements de l'huile provenant de la combustion. Dans cette étude, nous n'avons pas observé d'augmentation en teneur d'oxygène ou de l'indice d'acidité pour les huiles produites par

combustion, ce qui indiquerait que l'huile produite se trouvait assez loin du front de combustion. De plus, il n'y avait pas de changements marqués dans la teneur en soufre ou en azote. La résonance magnétique nucléaire (RMN) au proton (^{1}H) et au carbone-13 (^{13}C) n'indiqua que peu de changement dans l'aromaticité des composés, ce qui pourrait être attribué à des changements dans des fractions spécifiques de l'huile.

En général,les changements observés entre les huiles de production primaire et par combustion suggèrent que les éléments à point d'ébullition plus bas et qui se forment au front de la combustion par craquage thermique sont poussés en avant par les gaz de combustion et la vapeur. Ces éléments se condensent selon toute probabilité et se dissolvent dans l'huile, ce qui donne lieu à une réduction de leur viscosité et de leur densité et à une augmentation de leur teneur en naphta. Les huiles produites par récupération primaire et par combustion ont toutes deux montré une augmentation de leurs densité et viscosité dans les échantillons prélevés 18 mois plus tard.

Les changements observés dans cette étude suggèrent que les altérations de l'huile causées par le procédé de combustion n'affecteraient pas beaucoup le procédé de raffinage. Cette étude devrait être poursuivie sur une plus longue durée afin de déterminer les changements qui ont lieu lorsque le front de combustion se rapproche du puits de production.

INTRODUCTION

The steady decline in proven conventional oil deposits world wide has increased the emphasis on the use of heavy oil and bitumen. These deposits occur around the world; however, most if not all, share the common problem of having very little or no primary production. Each requires some form of production enhancement by reducing the viscosity of the oil to make it flow. The methods used generally involve heat and some combination of additives.

The properties of the oil in place and the reservoir characteristics are generally carefully studied to evaluate the potential of the deposit and to aid in the design of the recovery process. Many of these same characteristics are also used to evaluate the oil with respect to upgrading, refining and final usage.

Recovery processes vary from rather mild conditions for steam stimulation to quite extreme for combustion recovery. Depending upon the severity of the recovery process the recovered oil may be similar to the oil in the deposit or may be highly modified (oxidized or upgraded). Laboratory experiments (1-6) show that exposure of heavy oil to high temperatures from steam or in situ combustion results in cracking of the oil.

The commonly accepted model for in situ combustion is that when the oil in the reservoir is ignited the heat produced causes thermal cracking of the oil resulting in a laydown of coke on the sand. Very quickly after the start of the process the oil is pushed ahead of the firefront by the combustion gases and steam. The combustion process is sustained by burning of the coke. As the firefront proceeds a zone of thermal cracking of the oil in place precedes the firefront itself. Many mechanisms and reactions such as low temperature oxidation and dilution by condensation and dissolution of vaporized material can be expected as the oil moves ahead of the firefront. In fact reductions in viscosity and density are observed relatively early in the recovery process.

A Memorandum of Understanding was signed by the Governments of the United States of America, Canada, and the Provinces of Saskatchewan and Alberta to study different aspects of the problems related to the recovery of oil from heavy oil and tar sand deposits. One phase of the study is to determine the effects of different methods of in situ recovery on the composition of recovered bitumens and heavy oils and to investigate the analytical methods applicable to the study of the changes in the oil properties.

EXPERIMENTAL

Sampling Procedure

For the purpose of this study five samples of wellhead oil were obtained and analyzed from a deposit of heavy oil located in the Cummings formation of the Murphy Eyehill Field of Saskatchewan

operated by Murphy Oil Co. The sample collection and cleanup were carried out by the Petroleum Division of the Saskatchewan Research Council (SRC) and are described here. Two samples were obtained from each of a primary production well and a fireflood stimulated well. The first samples of each type were obtained approximately two years after production was started, and the second from the same wells, one year later. A sample was also obtained from a second fireflood well at the second sampling period.

Primary and fireflood wellhead samples were collected in a clean barrel over a period of 7 days, approximately 30 litres of sample each day.

Sample Cleaning Procedures

The drums were warmed before addition of demulsifier and before stirring. After stirring for 15 minutes, the heated contents, oil/emulsion/brine were left for 48 hours to cool and to allow the bulk of the water to separate from the oil. The primary sample was heated for 16 hours to raise the temperature from 20°C to 50°C. The fireflood sample was heated for 8 hours to raise the temperature from 20°C to 34°C.

The oil emulsions obtained from these drums were centrifuged using stainless steel centrifuge tubes equipped with gas tight caps. The primary wellhead sample was centrifuged for 3 hours at 45°C and 8500 r.p.m. The fireflood sample was centrifuged for 1.5 hours at 25°C and 8500 r.p.m. After centrifugation BS&W was determined on the recovered oil. The samples were diluted 50:50 with toluene in a graduated glass centrifuge tube, shaken on a wrist shaker for 10 min., followed by 20 min. centrifugation at 2000 r.p.m. The free water content was less than 0.1% by volume and no base sediment was found in any of the cleaned samples. The cleaned samples were stored in 1-litre polyethylene bottles with neoprene gasketed screw caps (wide mouth type).

Composition of the Produced Fluids (before clean-up)

A. **Primary Sample Well:**

Barrel: 2/3 full
demulsifier added to the barrel(Baker Chemicals D764): 30 ml. (275 ppm vol.)

BS&W results - barrel, volume percent

Free Oil	77%
Free water	3%
Emulsion	20% (3% oil and 17% H_2O)
Sediment	nil
TOTAL	100%

B: **Fireflood Sample Well**:

Barrel: full
demulsifier added (Baker Chemicals D764): 30 ml. (180 ppm vol.)

BS&W results - volume percent

Emulsion: 100%

Oil	47%
Water	53%
Sediment	nil
TOTAL	100%

Analytical Methods

Figure 1 shows a schematic of the analysis regime used on the samples to determine the various properties of the oil. Since the samples received from the cleanup procedure described were free of water and solids no further cleanup using solvent extraction was carried out.

The density of the whole oil was determined at 25°C using an Anton Parr Model DMA60 density meter with a DMA601 measuring tube capable of measuring to six decimal places. The instrument was thermostated using a recirculating water bath with a control accuracy of ±0.02°C. The temperature was monitored to the nearest 0.1°C.

The viscosity measurements were performed on a Brookfield Viscometer model RVT equipped with a cone and plate measuring head. The viscometer was maintained at the measuring temperatures of 25, 60 and 80°C using a water bath capable of controlling to ±0.2°C at the viscometer head.

The carbon, hydrogen, nitrogen, and oxygen analyses for most samples were performed on a Perkin-Elmer 240 Elemental Analyzer. Because of their low nitrogen content the middle distillate cut samples were analyzed using a Dohrman Chemiluminescence instrument. The sulfur in the whole oil samples was analyzed using the IP 242 method while that in the distillation cuts was analyzed using the ASTM D1552 procedure.

Distillation cuts of the oil were produced using a Nester Faust Spinning Band Distillation System. This system consists of a 480 mm x 7 mm column with a monel band spinning at approximately 29 rev/s. The distillation was operated at ambient pressure to 204°C at which point it was first brought to a vacuum of 5.0 mm and then 0.5 mm mercury for the remainder of the distillation. The distillations were performed at a reflux rate of 20:1 for the atmospheric portion and 5:1 for the distillation under vacuum conditions.

Simulated Distillations on the whole oil samples were carried out using the ASTM D-2 proposal P167 method run on a Hewlett Packard 5890 equipped with auto injection. The time slice data was collected on an HP3393 integrator and transferred to a VAX 11/750 computer for data processing. Simulated Distillation on the middle distillate cut was done using the ASTM D2887 procedure. Cetane Index calculations were made using D87 correlations to calculate the necessary data for inclusion in the CGSB83/9/28 proposed method.

The acid numbers were determined following a method based on the IP213 and IP177 methods using a Metrohm Model 636 Automatic titrator with a glass and Ag/AgCl reference electrode pair.

Olefin and diolefin content was measured following the UOP 326 method. The aromatics and olefin content of the naphtha cut was determined using the Fluorescence Indicator Method (FIA) ASTM D1319. The Conradson Carbon Residue was determined using a Micro Conradson Carbon Residue Analyzer according to ASTM 4530. Pour point measurements on the whole oil were performed according to ASTM D97.

The chromatographic SAPA type separations of the distillation cuts were performed using the method of Selucky (7) as modified by Wallace (8). After removal of the asphaltenes with pentane the rest of the sample was separated on a column 70 cm long x 1.5 cm dia., packed with 70-150 mesh Woelm Silica Gel using pentane to elute the saturates (fraction 1) and aromatics (fraction 2). Fraction 3 was then eluted with 15% toluene 85% pentane followed by 50% toluene, 50% pentane to obtain fraction 4. Fraction 5 is obtained with a mixture of 80% toluene, 10% diethylether and 10% methanol. The fractions are evaporated to dryness by letting them stand uncovered overnight in a fume hood. The remainder of the solvent from the last three fractions is removed by placing in an oven at 100°C for 10 minutes.

The Supercritical Fluid Chromatographic (SFC) determination of saturates, and aromatics on the distillation cuts was done using a 250 mm x 2.1 mm I.D. 5μ silica adsorbosphere column with supercritical CO_2 at 3600 psi as the carrier fluid (9).

The determination of the carboxylate content of the resins and asphaltene fractions was done according to the method described by Peterson (10), by differential infrared spectrometry (IR), on a Nicolet Model 5DX FTIR.

The proton and ^{13}C nuclear magnetic resonance (NMR) analysis was carried out using a Bruker WP80 NMR spectrometer.

Molecular weight distribution of the asphaltene fraction was done using a 60cm 10^3Å GPC column with methylene chloride as the eluting solvent.

Mass Spectral (MS) analyses were carried out on a Finnigan Mat 4500 Gas Chromatograph Mass Spectrometer. DB-5,Methyl Silicone or Hewlett Packard P.N.A capillary columns were used for the gas chromatographic separations. The Methyl Silicone column was 25 meters by 0.21 mm with .33μ film thickness. The DB-5 column was 30 meters by 0.25 mm with a 0.1μ film thickness. Split injection was used for sample injection on each capillary column. The first 5 minutes of the separation was isothermal at 65°C followed by temperature programming at 10°C per minute to 295°C. The helium carrier flow rate was 35 cm per second measured at 65 °C. The separations on the P.N.A. column were performed isothermally at 35°C for the first 10 minutes followed by 3°C per minute to 150°C, then 10°C per minute to 200°C. The helium carrier flow rate on this column was 27 cm per second measured at 65°C.

The mass spectra were obtained using 70 e.v. electron impact (EI) ionization or nitrous oxide (N_2O) chemical ionization (CI) as specified. The scan rate was generally 0.95 seconds to scan from 33 to 500 A.M.U.. Mass spectra were summed over the length of the chromatogram to give a picture of the types of chemical structures found in these samples.

The residue fraction samples were introduced into the mass spectrometer using the solids probe which was heated from 50°C to 300°C at 50°C per minute. The mass spectra were scanned from 150 to 650 AMU in 0.95 seconds and summed over the entire vaporization time. The EI mass spectra were obtained under the same conditions described above. The chemical ionization spectra were obtained using a Townsend discharge ionization source with N_2O at approximately 0.6 Torr at 120°C.

RESULTS AND DISCUSSION

Viscosity and density as shown in Table 1 are the first indication that the produced oil is somewhat "upgraded" as compared to the sample of primary production. It can be seen that the F-1 fireflood produced oils have a lower viscosity, C/H ratio, sulfur, metals content, carbon residue and pour point than those produced with no thermal stimulation. Small changes in viscosity and density can often be attributed to variations due to inhomogeneity in the reservoir, sampling or measurement error. Compared to primary production however, the rather large change in the viscosity of the fireflood F-1 samples from 1985 and 1987 is indicative of alteration of the oil.

The distillation data (Table 2) similarly indicates that the fireflood produced oil is lighter, with an almost ten fold increase in the naphtha content of the F-1 1985 sample. The naphtha content and reduction in residue boiling above 442°C of the two F-1 fireflood samples corresponds closely with the reduction in the density and viscosity. The F-1 1985 sample was altered considerably more than the sample taken in 1987 as indicated by all the measured properties. The F-2 sample from well 2

shows very little change from the primary production oil as indicated by these same parameters. It is of note that the 1987 sample P-1 from primary production shows a small increase in viscosity, density and distillation residue. This suggests that during the production, fractionation of the oil is occurring resulting in lighter oil produced early in production with the oil gradually becoming heavier with time. A similar fractionation may be occurring during fireflood production as we see by the increase of distillation residue in the F-1 1987 sample from well 1.

Partially oxidized oil with an increase in olefin content in the produced oil would be expected during in situ combustion. Material at the firefront would be altered by cracking and partial oxidation producing an increase in polar materials and acidic components. Oxygen content and acid number both actually show a slight decrease in the fireflood samples suggesting that the material was upgraded by dilution of light boiling materials being pushed ahead by the combustion front. The increase in acid number in the 1987 samples compared to 1985 is probably due to fractionation during movement through the formation since both primary and fireflood show a similar increase. The decrease in carbon residue in the fireflood samples also supports the theory of dilution of the bitumen by light materials. Laboratory scale fireflood simulation experiments by Gray (6) on Cold Lake bitumen showed increased oxygen content in the net produced oil due to oxidation of the oil, however a large fraction of the oxygen was in non-polar form and not as acidic functional groups.

The data in Tables 1 and 2 also show that both the primary and fireflood oils from 1987 are somewhat heavier than those sampled in 1985. The distillation data shows that the greatest change between 1985 and 1987 samples is observed in the amount of residue for both primary and fireflood samples. These results suggest that during production as the oil is moving through the reservoir it is fractionated, with some of the heavy components being retarded by the rock matrix. As more of the oil is produced these heavy components are produced at a higher concentration in the oil.

Except for the 1987 P-1 pour point, the pour point and the carbon residue data similarly follow this trend. This would suggest that during the life of a producing field gradually heavier and more difficult to process oil may be produced.

Naphtha Cut (boiling range 115 °C -204 °C)

Analysis of the naphtha cut shown in Table 3 clearly indicates that this fraction of the oil is dramatically changed by the fireflood process. Even though the nitrogen content is unchanged between the primary and fireflood produced samples and sulfur content only marginally lowered, there is a definite increase in the aromatic content as shown by FIA, SFC and MS. Even though there is a slight increase in the olefin content, by FIA, in the fireflood sample, an increase in diolefin

content expected from high temperature cracking is not observed in the 1985 sample. Diolefin content was not measured on the 1987 samples.

The total ion chromatograms obtained by GC-MS (Figure 2(A and B)) of the naphtha cut clearly show a shift to compounds of shorter retention time (or lower boiling point) in the fireflood production samples. This increase in concentration of these components could be attributed simply to vaporization of these materials near the firefront and carried by the combustion gases and steam front to the production well. The concentration of these components in the virgin oil, however. is very low. The chromatograms also clearly show the increase in lighter saturate molecules. The compounds found in the primary production are also present in the fireflood sample but are overshadowed by the presence of the lighter compounds.

The reconstructed ion chromatograms of the saturates, one ring saturates and aromatic compounds as identified by MS simplify the interpretation (Figures 3-5). The appearance of open chain saturates (by their characteristic regular pattern) is clearly seen in the reconstructed ion chromatogram for the saturates in the fireflood samples shown in Figures 3 (A and B). Figures 4(A and B) of the peaks attributed to one ring saturates show the appearance of smaller compounds (lower retention times) in the fireflood produced samples. Figures 5(A and B) show the peaks attributed to aromatic compounds as identified by MS.

The increase in lower molecular weight open chain saturates and aromatic molecules in the naphtha fraction suggests that the material pushed ahead of the firefront is composed of smaller molecules produced at the firefront by cracking of heavier material. Figures 6 (A and B) gives the distribution of the various compound types according to carbon number and clearly shows the relative increase in open chain saturates and alkyl benzene molecules in the fireflood produced oils. The naphtha cut of the primary produced oil is dominated by 1-ring and 2-ring naphthenes. The fireflood produced naphtha cut has a much greater proportion of alkyl benzenes especially toluene,ethyl and dimethyl benzene and a slight shift to smaller 1-ring naphthenes.

The presence of these smaller molecules clearly corresponds to the observed changes in the properties reported in Tables 1 and 2. The smaller change in the properties for well 2 is also seen in the reduced presence of the smaller molecules in the GC-MS.

Middle Distillate (204-345°C)

The middle distillate content of the oil did not change between primary and fireflood production in 1985 as seen in Table 2. The 1987 fireflood sample however does show an increase in middle distillate over that of the primary production. The change in the sulfur and nitrogen content from one year to the next is greater than the difference between the fireflood and primary samples and is

possibly affected by the repeatability of the distillation cut points. Since the gas oil contains a much larger quantity of nitrogen containing compounds a small shift in the distillation cut point can make a big difference to the nitrogen content of the middle distillate cut. Therefore, little significance can be attached to the nitrogen content changes in the middle distillate cut. The sulfur content in all five samples is very similar in this cut. The aniline point and cetane index provide a measure of the quality of the hydrocarbons for use as a stock for diesel fuels, and are both related to the aromatic content of the sample. A decrease in these parameters generally relate to a increase in aromatics content as shown by the data in Table 5 determined by SFC, column chromatography, proton and ^{13}C NMR. It should be noted that a different separation was obtained between fractions 2 and 3 in 1987 as compared to 1985. In 1987, fraction 2 consists primarily of mono aromatics while fraction 3 is predominantly di and tri aromatics. Table 6 gives the component type compositions obtained by MS using the Robinson method. Since all these component type separation methods provide very different information they should not be directly compared. It can be seen, however, that they all indicate increased aromatic content of the fireflood samples compared to the primary production. It is recognized that heavy oils are generally highly naphthenic in nature and that the higher molecular weight molecules often contain one or two aromatic rings with saturated substituents either as chains or more often as cyclic structures. During thermal cracking, many reactions are occurring simultaneously, producing a variety of compounds. From Table 6 it should be noted that paraffin and aromatic content generally increases with a corresponding decrease in naphthenic content going from primary production to the fireflood samples.

Chromatographic fractions 3, 4, and 5 were combined and analyzed by NMR for their aromatic nature as shown in Table 7. In contrast to the aromatics fraction (fraction 2) this polar fraction exhibits no change in proton aromaticity for the 1985 fireflood samples but shows a large decrease in ^{13}C aromaticity. The 1987 sample however has an increased proton aromaticity (increase from 49 to 67%) but still a decreased ^{13}C aromaticity. The relative increase in proton aromaticity relative to ^{13}C aromaticity suggests that either alkyl chains or naphthenic rings were removed from aromatic rings to be replaced by protons or non-substituted naphthenic rings were aromatized by the thermal process. Gray (6) reported a similar increase in the aromatic carbon bound to hydrogen especially in the resin I and asphaltene fractions of the oil. The sample from well 2 shows no change from the primary production.

Figures 7(A and B) show the GC-MS total ion chromatograms of the saturates fraction by GC-MS. Figures 8, 9 and 10 show the reconstructed ion chromatograms of the peaks representative of the open chain, one ring and two ring naphthenic compounds for the 1987 samples. The shift in masses at the different carbon numbers as seen in the summed mass spectra shown in Figure 11 demonstrates the shift from ringed alkanes in the primary production to open chain alkanes in the

fireflood produced oil. Mass 181 represents the $C_{13}H_{26}$ single ring naphthenic structure. From this figure, we can see that the major peaks in the primary production sample are 179 and 181 representing the double and single ring naphthenics respectively with a minor contribution from the normal paraffin and the triple ring naphthenic. The fireflood sample, however, shows a large increase in the mass 183 peak representing the C_nH_{2n+2} or normal paraffin which must have been produced at the firefront by cracking of the naphthenic material or breaking of paraffinic side chains off aromatic or naphthenic molecules. A similar change in the pattern is found at other C numbers. The regular pattern of straight chain alkanes is evident in the reconstructed ion chromatogram for the open chain alkanes in Figure 8 for the F-1 sample.

The distribution of saturate compounds in the middle distillate as shown in Figure 12 does not change appreciably between the primary and fireflood except for the increase in the open chain molecules C12 to C15. These are probably formed by thermal cleavage from larger molecules near the firefront. A shift to lower carbon numbers is observed for both fireflood and primary samples between the 1985 and 1987 samples which is probably attributable to a slight change in the cut point during the distillation.
The total ion chromatograms of the aromatic fraction of the middle distillate cut shows an increase in smaller aromatic molecules (lower retention times) as seen in figures 13 A and B. The 1985 samples were spiked with D_8 naphthalene to give a reference marker for comparison purposes.

Figures 14,15,16 and 17 show the reconstructed ion chromatograms of the peaks attributable to alkyl benzenes, benzocyclo paraffins, benzo dicyclo paraffins and the fluorenes/anthracenes respectively in the 1987 samples. There is a dramatic increase in the smaller molecules in each of these series of compounds in the fireflood samples. The distribution of compounds in this fraction shown in figure 18 clearly reflects this shift to smaller molecules. The 1985 sample shows the presence of naphthalene compounds which is the result of a different chromatographic separation between fraction 2 and fraction 3. The sample from well 2 shows minimal changes due to the fireflood process. There is a dramatic shift to higher carbon numbers in each group of compounds from 1985 to the 1987 sample. This change is probably due to a chromatographic type of separation in the formation as the oil moves toward the production well.

As seen above, fraction 2 from the chromatographic separation consists primarily of mono aromatic compounds. Fraction 3, though containing some mono aromatics contains most of the di and tri aromatics. Figures 19 (A and B) show the total ion chromatograms for this fraction and indicate the appearance of peaks of lower boiling compounds in the fireflood samples compared to the primary production. Figures 20(A and B) which give the distribution of compound types shows the relative increase in some of the naphthalenes.

This data indicates that the middle distillate fraction is somewhat upgraded by the fireflood recovery process with an increase in aromatics content. This change may slightly reduce the quality of this cut for use as a stock for diesel fuel. Other changes to this cut are probably insignificant.

Gas Oil Cut (345-442°C)

Data on the Gas oil distillation cut is given in Table 8 showing the nitrogen and sulfur content and the saturates and aromatics by SFC, proton NMR and ^{13}C NMR. SFC shows some increase in molecules containing aromatics in the 1985 fireflood production; however, NMR indicates that there is no significant change in total aromaticity of these samples. The 1987 samples show little or no change between primary and fireflood production.

The nitrogen content is somewhat higher in the fireflood production in 1985, but lower in 1987 and in fact greater differences are observed between the 1985 and 1987 samples. No change is observed in the sulfur content. No differences in the aromaticity (Table 9) of the individual chromatographic fractions were measured by NMR. The apparent inconsistency between the chromatography and NMR can be explained as follows. If the molecules identified as aromatics in the primary by chromatography contain many aliphatic or naphthenic substituents, but in the fireflood contain fewer substituents due to cracking, the aromaticity as measured by NMR will remain essentially the same. This is so since NMR measures the total aromatic carbon (or hydrogen) which would not change provided side chains are merely removed.

Figure 21 shows the distribution of compound types by mass spectral analysis of the saturates fraction of the gas oil distillation cut by chemical ionization. No differences between the primary production and fireflood samples were observed.

Figures 22 and 23 show the mass spectral analysis of the aromatics fraction (fraction 2) and fraction 3 of this material respectively. Again no significant differences are observed between the primary and fireflood samples.

Distillation Residue (> 442°C)

The analyses of the whole distillation residue are presented in Table 10. The data indicates little change in the nitrogen, sulfur and carbon residue due to the fireflood recovery process. The differences between the 1985 and 1987 samples are greater than between primary and fireflood production. The chromatographic separation also indicates little change. This material is very viscous and consequently it is difficult to remove the last traces of the solvents used in the chromatographic separation which results in a total recovery of over 100% for some of the samples.

Table 11 shows the NMR data for the chromatographic fractions. The proton and C^{13} aromaticities are not consistent. At this time, no explanation can be provided.

The residue due to its polar nature and low volatility was not introduced into the MS via a gas chromatograph but was introduced by vaporization from the solids probe. No noticeable differences were observed in the mass spectra of either the 1985 or 1987 samples. Figures 24,25 and 26 show the compound distribution by MS for the saturates fraction (cut 1), the aromatics (fraction 2), and fraction 3 of the 1987 distillation residue.

Figure 27 shows the gel permeation chromatograms of the asphaltenes which indicate no difference in molecular size distribution between the two samples. Even though the asphaltene content of the residue cuts is slightly lower in the fireflood samples, no differences could be measured in the molecular weight distribution of the asphaltenes by gel permeation chromatography.

Table 12 shows concentrations of free carboxylate salts, the silyl esters and anhydrides measured in the various fractions following the method of Peterson (10). The low measured concentrations of these species in each of the samples and the similarity of concentrations between the primary production and fireflood samples indicate once again that the differences in the two samples are very minor. No evidence is shown for oxidative production of polar species as would be expected for a fireflood production sample. The accuracy of the method to measure these species in samples such as these is difficult to ascertain, however, any concentrations measured below approximately 10^{-3} mole/liter can only be considered as an indication that the concentration of the species is very low. These minor differences are consistent with the column chromatographic data which show no increase in polars components in the fireflood produced oil. These results are also consistent with the acid number data shown in Table 2.

CONCLUSIONS

The density, viscosity and distillation analyses provided the most rapid and sensitive indicators of changes in the oil quality. Column chromatography followed by GC/MS provided valuable information on changes in specific component types. The data provided by the column chromatographic separations by themselves is more difficult to reproduce and hence not that useful in interpreting changes. Elemental analysis, acid number and NMR are potentially useful analyses; however, in the present study little change was observed in these quantities between primary and fireflood oils.

Overall the largest changes as a result of the fireflood production process show up primarily in the naphtha and middle distillate cuts. The differences that are observed appear to be explained by the production of volatiles which move ahead of the firefront diluting the produced oil. This phenomenon is not unexpected during the early stage of the fireflood. Samples much closer to the firefront not

analyzed in this study are expected to be modified more by the higher temperature and presence of oxygen. Thermal cracking near the firefront produces an increase in smaller and volatile paraffinic, naphthenic and aromatic compounds that are found in the naphtha and middle distillate cuts.

The observed changes in physical properties correspond well with the changes in compound composition determined by GC-MS. The expected elemental changes such as oxidation and increased olefin and diolefin content expected to be prominent in fireflood production were not observed. It would be expected that as the firefront approaches a production well such changes in oil composition would be evident.

The composition changes produced by the fireflood process observed in this limited study would not be expected to affect the processability of the crude. It would be expected that pooling of oil from multiple wells at the production field would produce a crude oil of relatively stable composition with intermediate properties. Without more extensive studies over the life time of a process, it is difficult to predict what proportion of the oil produced will be altered appreciably to affect the refining process. From this study over a period of approximately two years, the observed changes could only be attributed to dilution of the oil produced by light materials vaporized or produced by thermal cracking at the firefront and pushed ahead of the front by the steam and combustion gases.

ACKNOWLEDGEMENTS

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We also wish to thank Murphy Oil for kindly providing their production samples for this study. We also want to thank the technologists of the Analytical Service Laboratory of the Oil Sands and Hydrocarbon Processing Department for their hard work in this study. We thank Marv Rawluk and Wendy Wade from the Analytical Lab in the Materials Testing Department for their effort in providing the Mass Spectral and NMR data in this project.

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TABLE 1: WHOLE OIL ANALYSIS

	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
DENSITY g/ml@ 25°C	0.9724	0.9228	0.9735	0.9415	0.9724
VISCOSITY 25.2°C	3190.0	55.7	3340.0	280.0	2880.0
cPs 60°C	218.0	16.3			
80°C	8.0	9.4			
CARBON wt.%	84.8	84.7	85.0	85.3	85.0
HYDROGEN	10.9	11.4	10.9	11.5	10.8
NITROGEN	0.4	0.3	0.4	0.4	0.4
OXYGEN	0.9	1.0	0.8	0.7	0.7
SULFUR	3.25	2.8	3.3	2.9	3.3
ASH	0.02	0.02	0.06	0.04	0.09
	100.27	100.22	100.46	100.84	100.29
NICKEL mg/kg	36.5	24.5	64.0	56.0	66.0
VANADIUM	101.0	53.0	112.0	85.0	114.0
IRON	0.7	0.2	5.3	6.2	110.0

TABLE 2: WHOLE OIL ANALYSIS

	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
ACID NUMBER mg KOH/g	1.05	0.8	1.63	1.48	2.98
CARBON RESIDUE wt.%	10.5	7.2	10.8	8.2	10.7
POUR POINT °C	-3.0	-42.0	-15.0	-33.0	-12.0
DISTILLATION					
Vol %					
NAPHTHA 115-204°C	2.6	25.2	3.0	14.2	4.9
MIDDLE DIST. 204-345°C	23.6	23.3	19.8	24.1	19.5
GAS OIL 345-442 °C	18.4	13.4	15.0	13.0	14.7
RESIDUE 442 °C	55.4	38.1	62.2	48.7	60.9

Simulated Distillation

% Off	Temp Deg°C	
0.5	143	112
5	223	174
10	262	206
15	293	231
20	320	259
25	346	290
30	372	323
35	397	357
40	422	391
45	445	427
50	471	462
55	501	507
59.7	539	540

TABLE 3: NAPHTHA CUT 115-204°C

		PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
	NITROGEN mg/kg	9.9	9.9	<1.0	4.0	<1
	SULFUR wt.%	0.36	0.31	0.47	0.37	0.55
FIA	AROMATICS vol%	5.7	25.2	6.2	21.6	15.2
	OLEFINS vol%	0.6	1.8	1.4	1.6	2.4
SFC	ALIPHATICS vol%	96.0	72.0	91.0	69.4	82.3
	AROMATICS	4.0 wt.%	28.0 wt.%	8.5	30.6	17.7
MASS SPEC	SATURATES %	98.0	67.0	97.0	74.0	71.0
	AROMATICS %	2.0	33.0	3.0	26.0	29.0
TITRATION						
	DIOLEFIN	0.74	0.30			

TABLE 4: MIDDLE DISTILLATE

	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
Nitrogen mg/Kg	41.3	96.1	8.0	43.0	7.0
Sulfur wt.%	1.36	1.37	1.29	1.25	1.30
Density gms/ml	0.8883	0.8957	0.8861	0.8902	0.8875
Aniline Pt.	51.0	43.3	50.05	45.75	50.95
Cetane Index	36.7	32.7	35.2	35.0	35.6
Viscosity csts	3.909	3.463			

TABLE 5: MIDDLE DISTILLATE

		PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
SFC	Saturates	66.8	60.6	64.1	56.6	62.8
	Aromatics	33.2	39.4	37.2	43.4	37.2
PROTON NMR						
	ALIPHATIC	95.0	93.0	96.0	93.0	96.0
	AROMATIC	5.0	7.0	4.0	7.0	4.0
^{13}C NMR						
	ALIPHATIC	87.0	78.0	85.0	79.0	84.0
	AROMATIC	13.0	22.0	15.0	21.0	16.0

CHROMATOGRAPHIC SEPARATION	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
Fraction 1 saturates	58.5wt.%	54.7	61.7	59.0	60.1
Fraction 2 aromatics 1	26.7	30.0	13.7	18.5	12.4
Fraction 3 aromatics 2	12.5	9.6	22.0	18.9	23.0
Fraction 4 polars 1	0.1	0.2	1.4	0.5	3.3
Fraction 5 polars 2	0.5	0.6	<0.1	<0.1	<0.1
ASPHALTENES	<0.1	<0.1	<0.1	<0.1	<0.1
	98.4	95.2	98.8	97.1	98.8

TABLE 6: MASS SPECTRAL ANALYSIS OF THE MIDDLE DISTILLATE CUT (by Robinson Method) done at CANMET

	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
Saturates	64.8	57.8	74.3	69.8	71.2
Paraffins	8.3	11.7	11.5	15.2	13.6
1-ring	24.7	20.3	25.2	22.3	24.5
2-ring	19.0	17.1	24.6	19.4	21.5
3-ring	12.6	8.5	12.8	12.8	11.4
Aromatics	35.1	42.1	25.6	30.1	28.7
mono					
Benzenes	4.6	5.8	3.8	5.6	4.6
Naphtheno benzenes	6.7	7.2	6.6	7.1	6.6
Dinaphtheno benzenes	5.1	5.5	4.8	4.1	5.0
	16.4	18.5	15.2	16.8	16.2
di					
Naphthalenes	6.2	9.5	2.0	4.1	2.0
Acenaphthenes,etc	4.4	4.4	3.7	3.4	3.9
Fluorenes	2.6	2.6	1.8	1.8	3.1
	13.2	16.5	7.5	9.3	9.0
tri					
Phenanthrenes	1.2	1.3	0.0	0.7	0.7
naphthene phenanthrenes	0.6	0.1	0.1	0.0	0.1
	1.8	1.4	0.1	0.7	0.8

TABLE 6: Continued

	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
tetra					
Pyrenes	0.5	0.5	0.1	0.0	0.2
Chrysenes	0.1	0.2	0.1	0.0	0.0
	0.6	0.7	0.2	0.0	0.2
Thiopheno					
Benzothiophenes	1.6	2.4	1.6	2.0	1.5
Dibenzo-thiophenes	0.6	1.1	0.2	0.8	0.4
Naphthobenzo thiophenes	0.2	0.9	0.0	0.0	0.0
	2.4	4.4	1.8	2.8	1.9

TABLE 7: MIDDLE DISTILLATE 204 - 345°C

	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
PROTON NMR					
Combined fractions 3, 4 & 5					
Aliphatic	84.0	85.0	83.0	69.0	84.0
Aromatic	16.0	15.0	17.0	31.0	16.0
^{13}C NMR					
Combined fractions 3, 4 & 5					
Aliphatic	52.0	78.0	51.0	33.0	54.0
Aromatic	48.0	22.0	49.0	67.0	46.0

TABLE 8: GAS OIL 345 - 442°C

		PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
NITROGEN mg./kg		774.0	908.0	660.0	371.0	378.0
SULFUR wt.%		2.63	2.44	2.31	2.44	2.34
SFC	SATURATES	39.7	30.8	39.5	39.4	41.5
	AROMATICS	60.3	69.25	60.5	60.6	58.5
PROTON NMR	ALIPHATICS	94.0	93.0	93.0	92.0	93.0
	AROMATICS	6.0	7.0	7.0	8.0	7.0
^{13}C NMR	ALIPHATICS	76.0	76.0	76.0	77.0	77.0
	AROMATICS	24.0	24.0	24.0	23.0	23.0
Fraction 1 saturates		38.3	37.4	39.6	37.8	40.4
Fraction 2 aromatics		18.5	30.0	16.8	16.0	15.1
Fraction 3 aromatics		35.3	26.4	35.9	36.3	34.9
Fraction 4 polars		3.8	2.4	4.2	4.9	4.2
Fraction 5 polars		4.0	3.3	4.7	2.1	4.5
ASPHALTENES		<0.1	<0.1	<0.1	<0.1	<0.1
		99.9	99.6	93.9	97.1	99.1

TABLE 9: GAS OIL 345 - 442°C

		PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
Proton NMR						
Fraction 3	Aliphatic	86*	84*	86	84	83
	Aromatic	14*	16*	14	16	17
Fraction 4	Aliphatic			79	78	83
	Aromatic			21	22	17
Fraction 5	Aliphatic			90	87	88
	Aromatic			10	13	12
C_{13} NMR						
Fraction 3	Aliphatic	51*	52*	56	53	52
	Aromatic	44*	48*	44	47	48
Fraction 4	Aliphatic			46	42	50
	Aromatic			54	58	50
Fraction 5	Aliphatic			62	56	59
	Aromatic			38	44	41

* Fractions 3, 4, & 5 COMBINED - POLARS

TABLE 10: RESIDUE - 442°C

CHROMATOGRAPHIC SEPARATION	PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
Fraction 1 saturates	14.5	14.0	13.1	15.9	21.9
Fraction 2 aromatics	10.1	9.5	15.7	11.8	9.2
Fraction 3	26.7*	27.0*	28.4	20.6	22.4
Fraction 4	15.6*	18.6*	9.5	11.1	10.4
Fraction 5	18.8*	18.1*	13.3	19.0	12.9
ASPHALTENES	19.5	17.4	19.7	17.4	21.3
	105.2	104.6	99.7	95.8	98.1
NITROGEN mg/kg	5694.0	5749.0	4100.0	4800.0	4300.0
SULFUR wt%	4.34	4.11	4.11	4.08	4.24
CARBON RESIDUE wt%	18.37	18.22	17.87	17.1	17.47

*traces of solvent left in these fractions

TABLE 11: RESIDUE - 442°C

		PRIMARY P-1;85/11	FIREFLOOD F-1;85/11	PRIMARY P-1;87/5	FIREFLOOD F-1;87/5	FIREFLOOD F-2;87/5
Fraction 3	Aliphatic	91	89	90	93	90
	Aromatic	9	11	10	7	10
Fraction 4	Aliphatic	89	90	88	87	87
	Aromatic	11	10	12	13	13
Fraction 5	Aliphatic	92	92	91	91	91
	Aromatic	8	8	9	9	9
Asphaltenes	Aliphatic	88	87	89	88	89
	Aromatic	12	13	11	12	11
C_{13} NMR						
Fraction 3	Aliphatic	56	65	65	72	64
	Aromatic	44	35	35	28	36
Fraction 4	Aliphatic	56	59	55	55	53
	Aromatic	44	41	45	45	47
Fraction 5	Aliphatic	66	64	62	65	62
	Aromatic	34	36	38	35	38
Asphaltene	Aliphatic	62	49	51	50	50
	Aromatic	38	51	49	50	50

Table 12

SAMPLE NAME	FREE CARBOXYLIC ($molL^{-}$)	SILYL ESTERS ($molL^{-}$)	ANHYDRIDES ($molL^{-}$)	CARBOXYLIC SALTS ($molL^{-}$)
MIDDLE DISTILLATE, COMBINED Fractions 3,4 & 5:				
Primary P-1;85/11	1.0×10^{-2} (0.11678 g)	1.8×10^{-2} (0.09342 g)	-Insufficient- Sample	8.0×10^{-3}
Fireflood F-1;85/11	-Insufficient sample to do any analyses-			
GAS OIL, COMBINED Fractions 3,4 & 5:				
Primary P-1;85/11	2.8×10^{-3} (0.18037 g)	9.6×10^{-3} (0.14430 g)	-poor peaks-	6.8×10^{-3}
Fireflood F-1;85/11	2.8×10^{-3} (0.12695 g)	9.6×10^{-3} (0.10156 g)	-poor peaks-	6.8×10^{-3}
Fraction 3 - RESIDUE:				
Primary P-1;85/11	-no peak- (0.08964 g)	4.8×10^{-5} (0.07171 g)	-poor peaks-	4.8×10^{-5}
Fireflood F-1;85/11	-no peaks obtained for any analyses** -			
Fraction 4- RESIDUE:				
Primary P-1;85/11	-no peaks obtained for any analyses** -			
Fireflood F-1;85/11	4.0×10^{-5} (0.13856 g)	1.1×10^{-3} (0.11084 g)	6.0×10^{-4} (0.20690 g)	1.1×10^{-3}
Fraction 5- RESIDUE:				
Primary P-1;85/11	1.8×10^{-3} (0.04212 g)	2.0×10^{-2} (0.03370 g)	7.4×10^{-4} (0.14514 g)	1.8×10^{-2}
Fireflood F-1;85/11	2.6×10^{-3} (0.14158 g)	2.6×10^{-5} (0.11326 g)	1.0×10^{-1} (0.15126 g)	
ASPHALTENES - RESIDUE:				
Primary P-1;85/11	2.6×10^{-4} (0.10754 g)	1.2×10^{-3} (0.08603 g)	-poor peaks-	9.4×10^{-4}
Fireflood F-1;85/11	5.1×10^{-4} (0.10347 g)	1.7×10^{-3} (0.08278 g)	-poor peaks-	1.2×10^{-3}

FIGURE 1

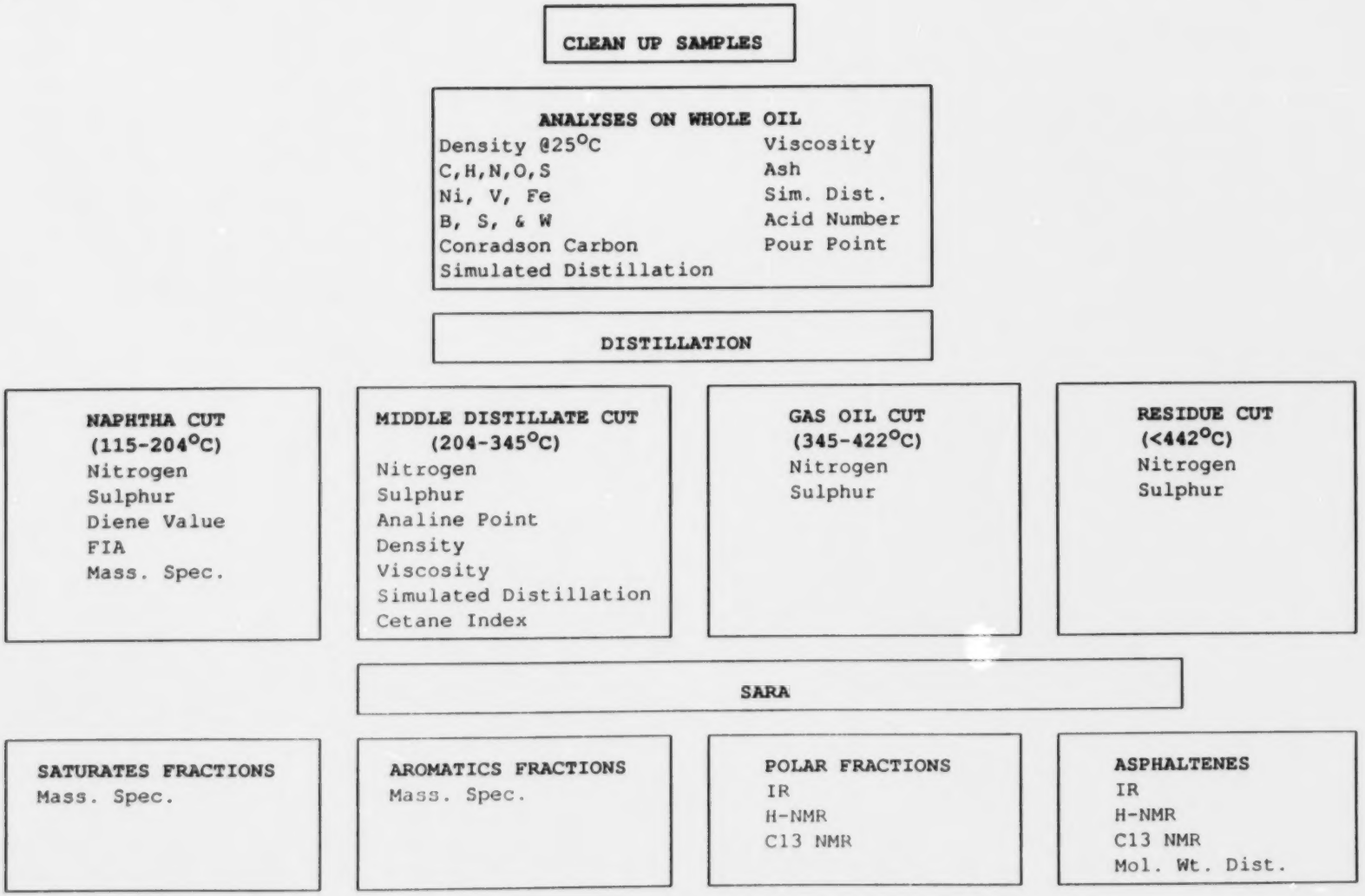
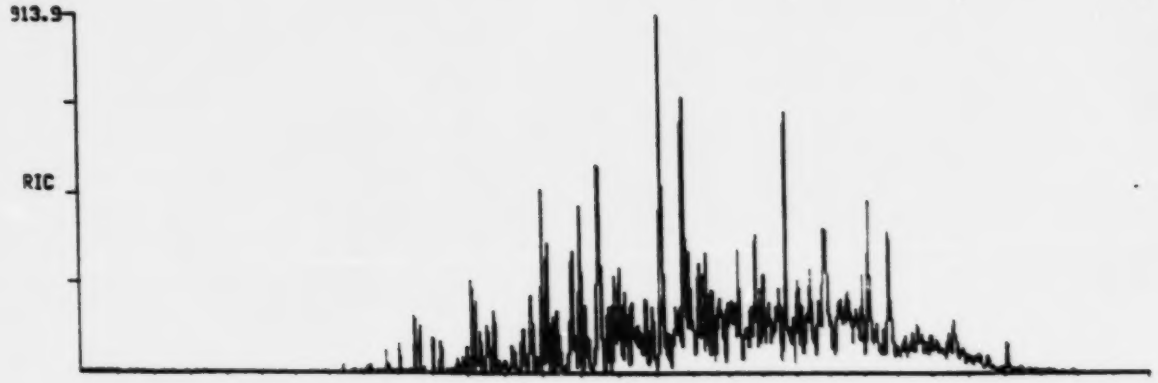

CLEAN UP SAMPLES
ANALYSES ON WHOLE OIL
Density @25°C
C,H,N,O,S
Ni, V, Fe
B, S, & W
Conradson Carbon
Simulated Distillation
Viscosity
Ash
Sim. Dist.
Acid Number
Pour Point
DISTILLATION
NAPHTHA CUT
(115-204°C)
Nitrogen
Sulphur
Diene Value
FIA
Mass. Spec.
MIDDLE DISTILLATE CUT
(204-345°C)
Nitrogen
Sulphur
Analine Point
Density
Viscosity
Simulated Distillation
Cetane Index
GAS OIL CUT
(345-422°C)
Nitrogen
Sulphur
RESIDUE CUT
(<442°C)
Nitrogen
Sulphur
SARA
SATURATES FRACTIONS
Mass. Spec.
AROMATICS FRACTIONS
Mass. Spec.
POLAR FRACTIONS
IR
H-NMR
C13 NMR
ASPHALTENES
IR
H-NMR
C13 NMR
Mol. Wt. Dist.

Figure 2 (A)

The total ion chromatograms of the Naphtha Cut of the 1985 Primary and Fire Flood Production samples.

PRIMARY
P-1; 85/11



FIRE FLOOD
F-1; 85/11

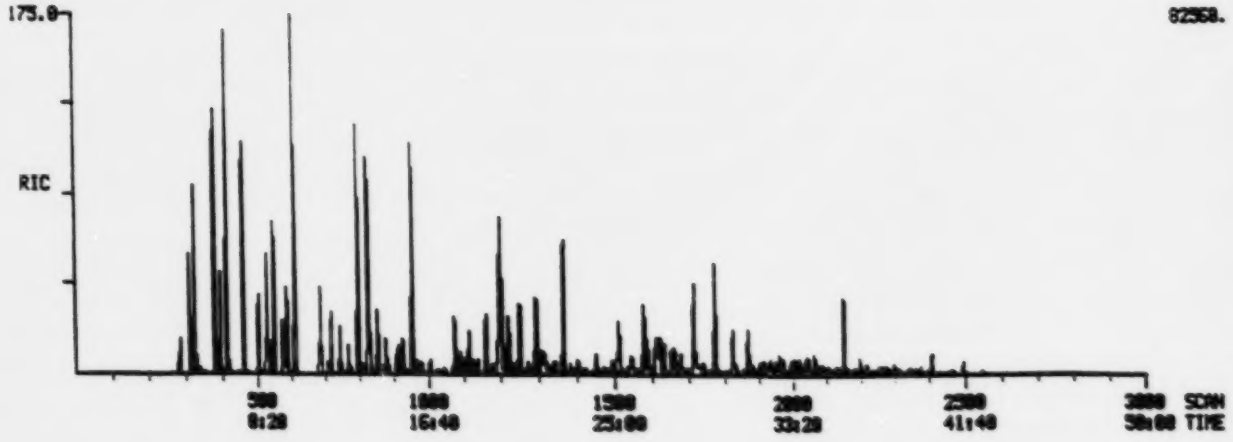
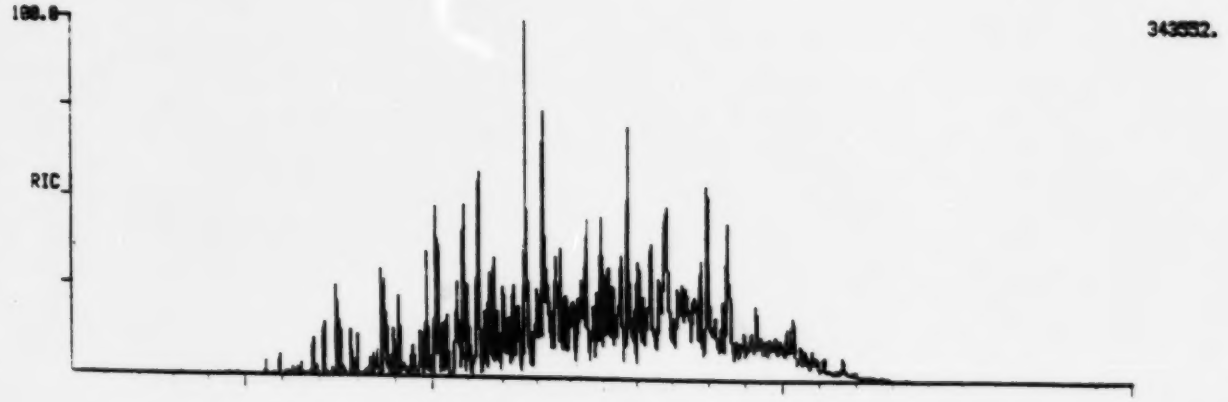


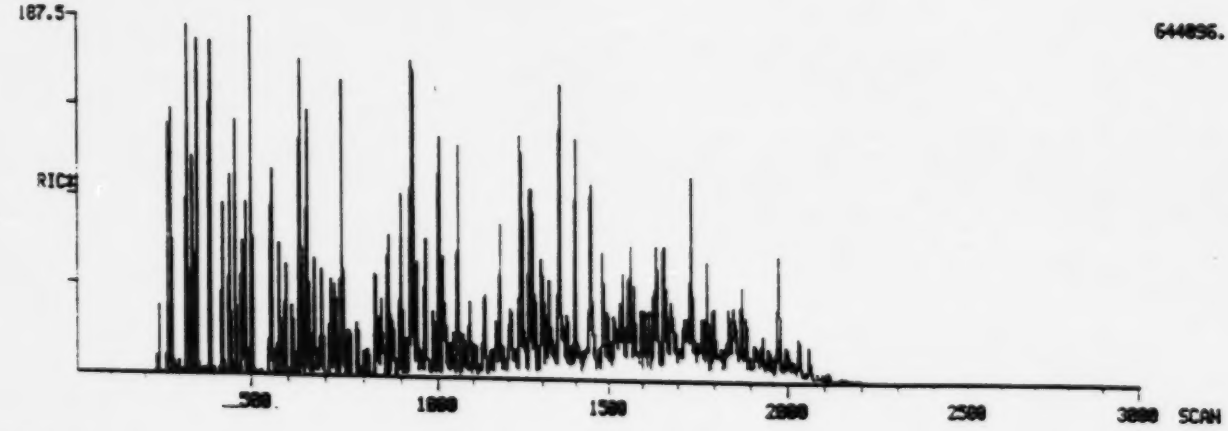
Figure 2 (B)

The total ion chromatograms of the Naphtha Cut of the 1987 Primary and Fire Flood Production samples.

PRIMARY
P-1; 87/5



FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5

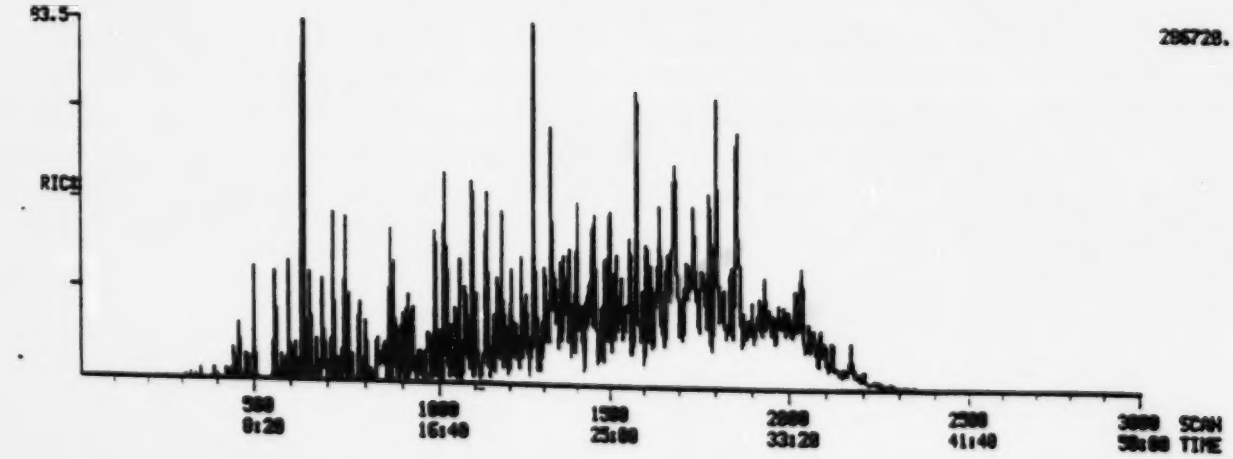
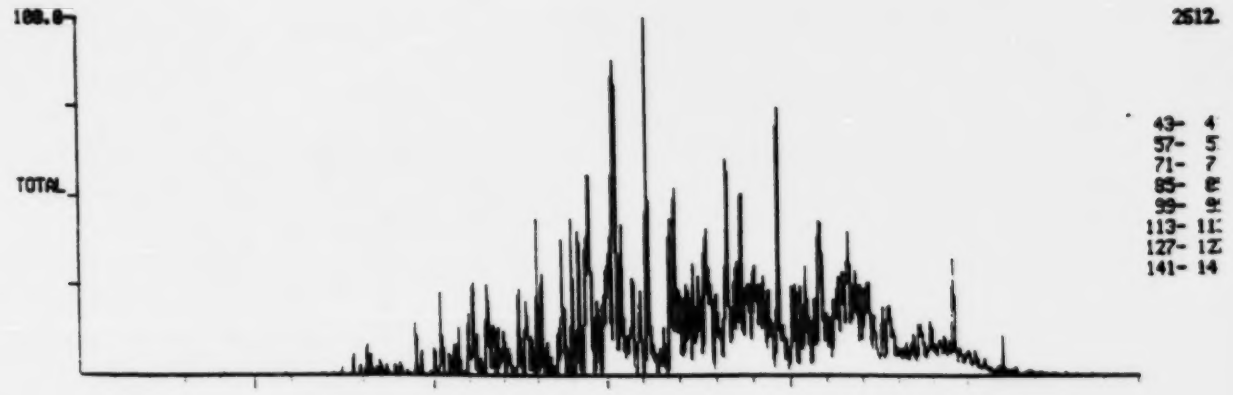


Figure 3 (A)

The reconstructed ion chromatograms for saturates in the Naphtha Cut of the 1985 primary and fire flood production samples.

PRIMARY
P-1; 85/11



FIRE FLOOD
F-1; 85/11

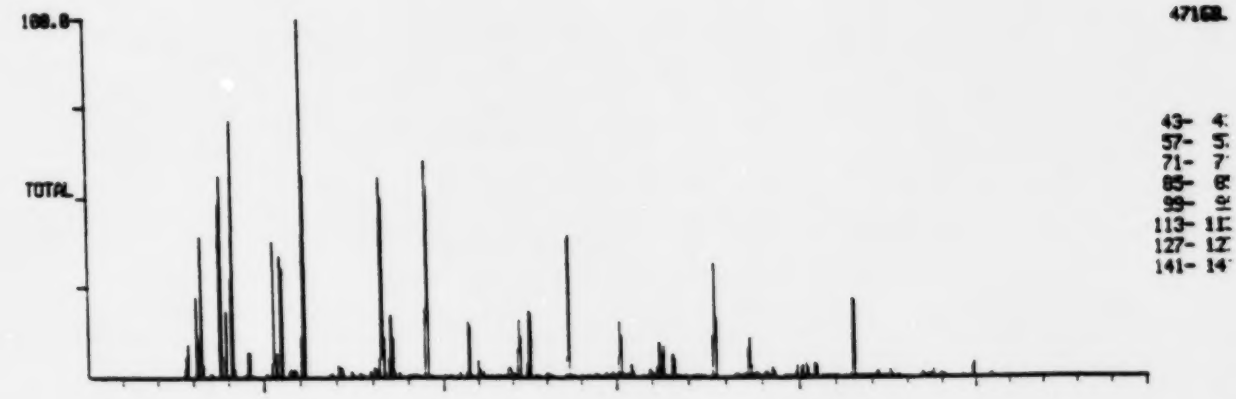
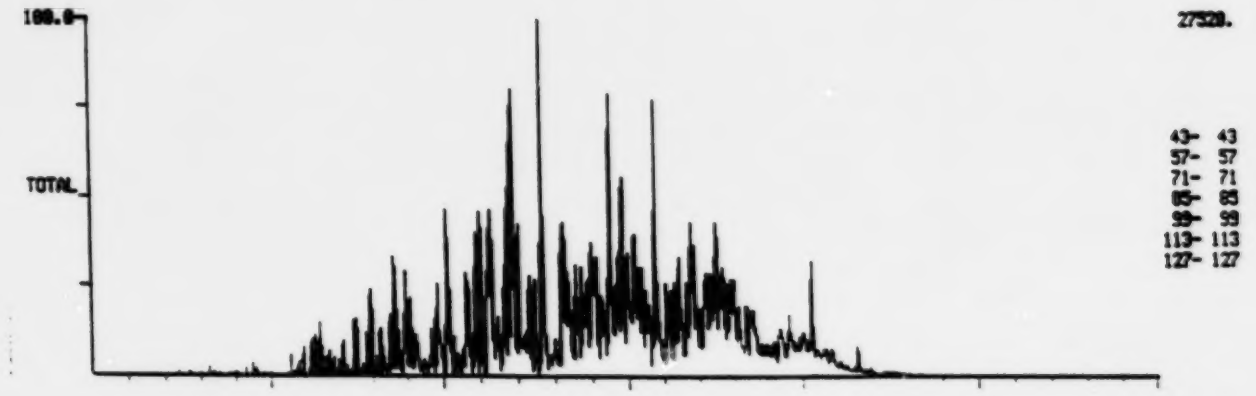


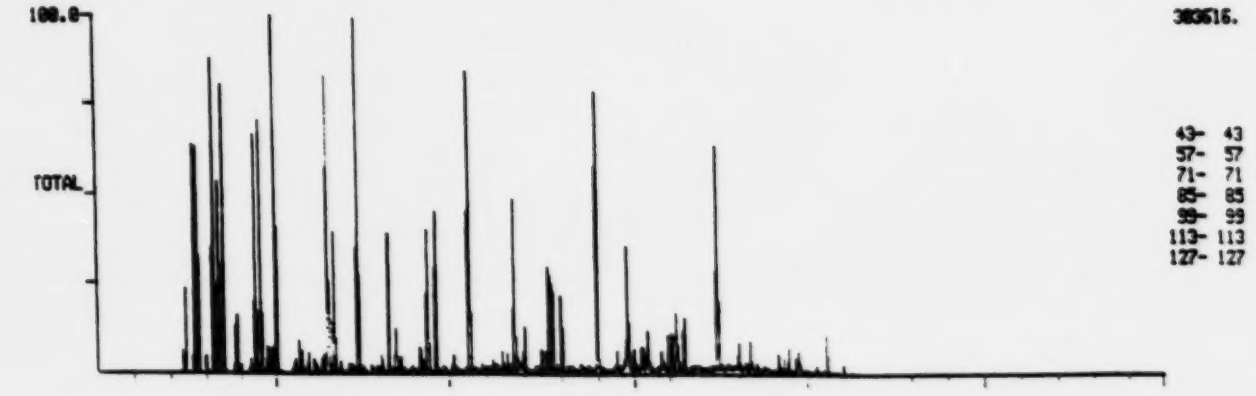
Figure 3 (B)

The reconstructed ion chromatograms for saturates in the Naphtha Cut of the 1987 primary and fire flood production samples.

PRIMARY
P-1; 87/5



FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5

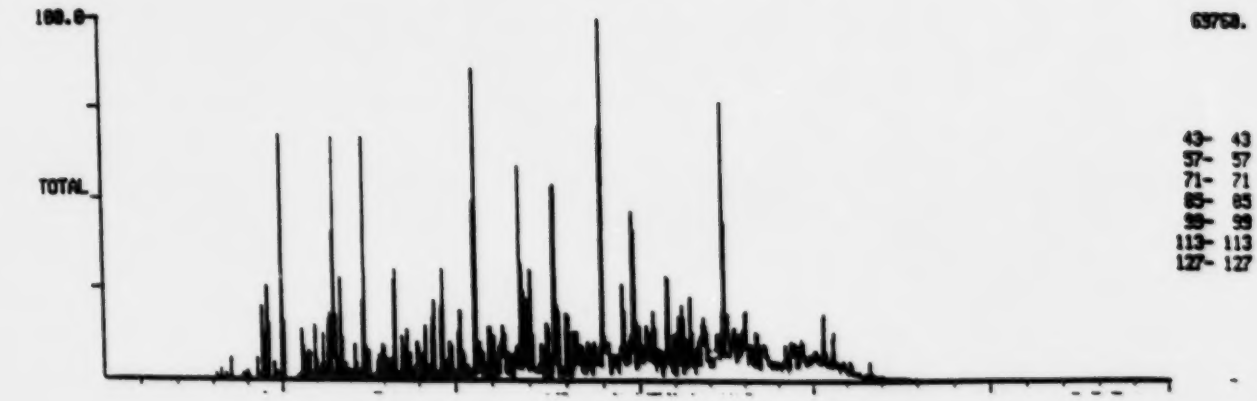
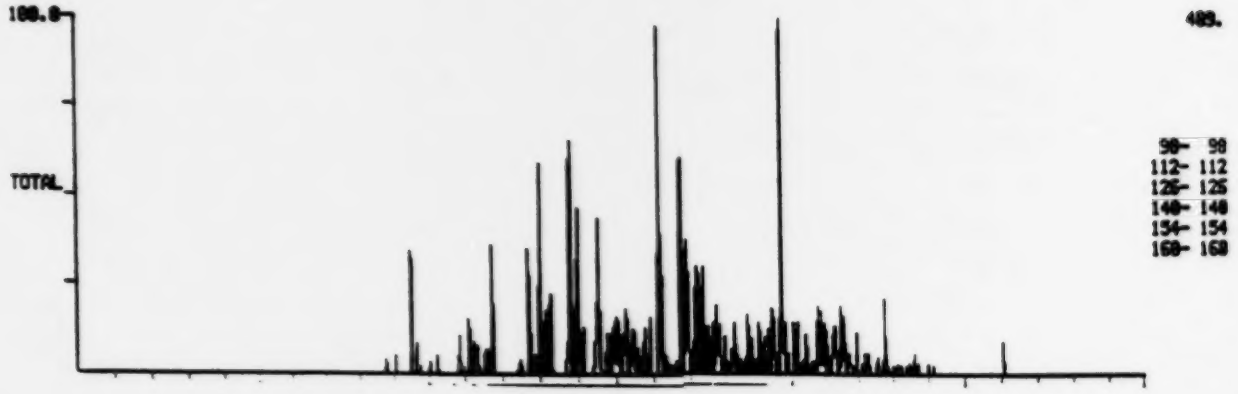


Figure 4(A)

The reconstructed ion chromatograms for the one ring saturate compounds found in the Naphtha Cut of the 1985 primary and fire flood production samples.

PRIMARY
P-1; 85/11



FIRE FLOOD
F-1; 85/11

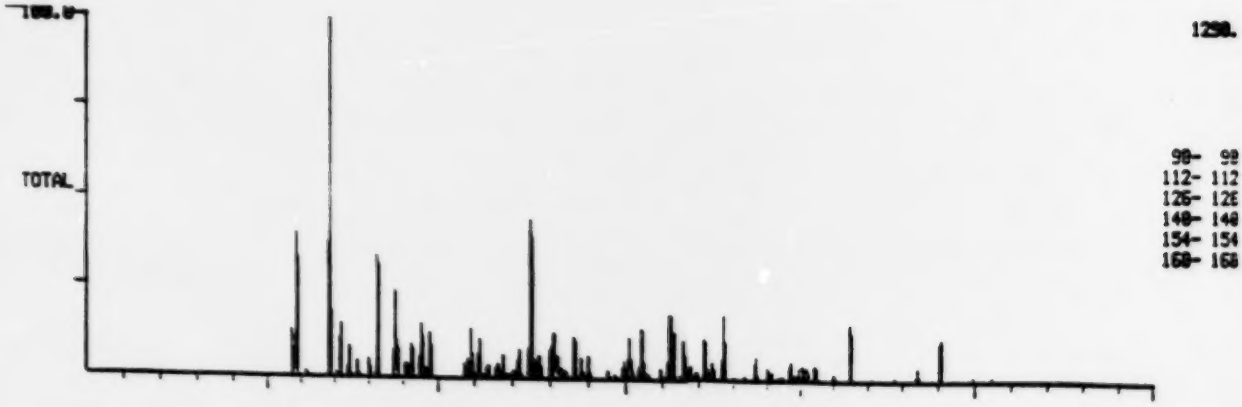
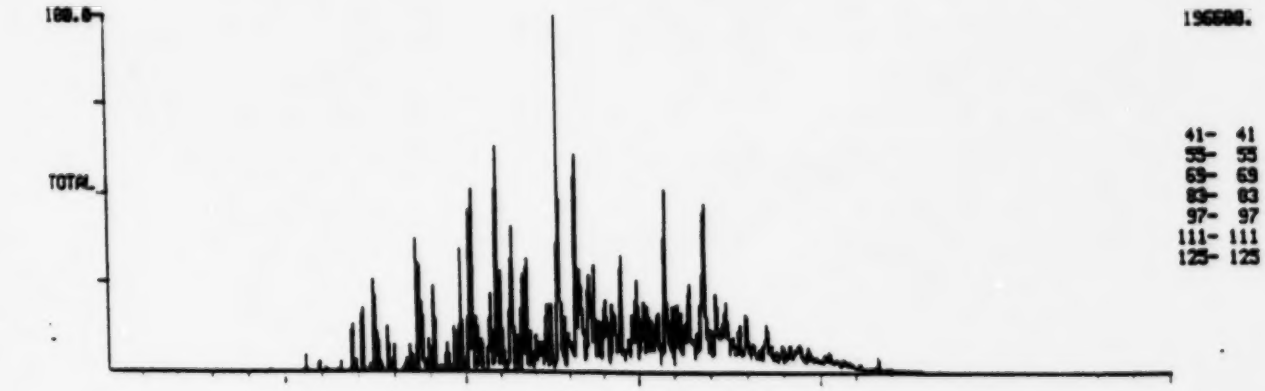


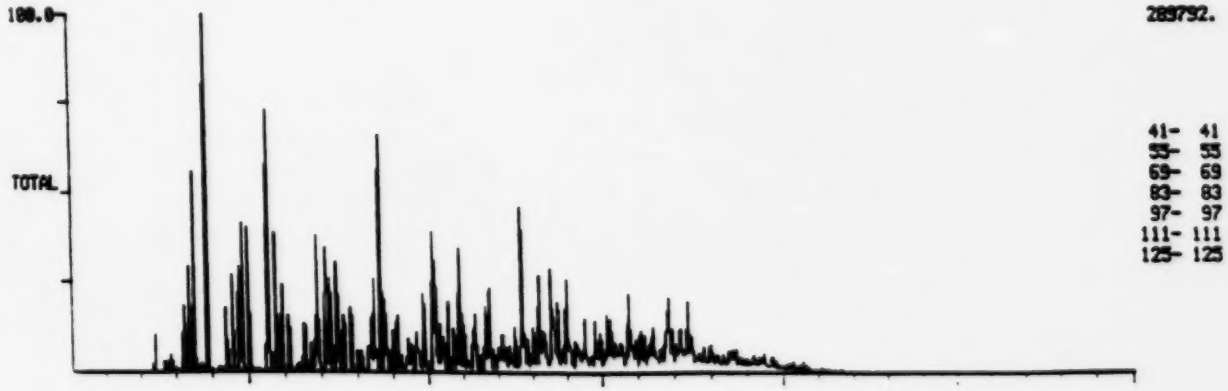
Figure 4(b)

The reconstructed ion chromatograms for the one ring saturate compounds found in the Naphtha Cut of the 1987 primary and fire flood production samples.

PRIMARY
P-1; 87/5



FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5

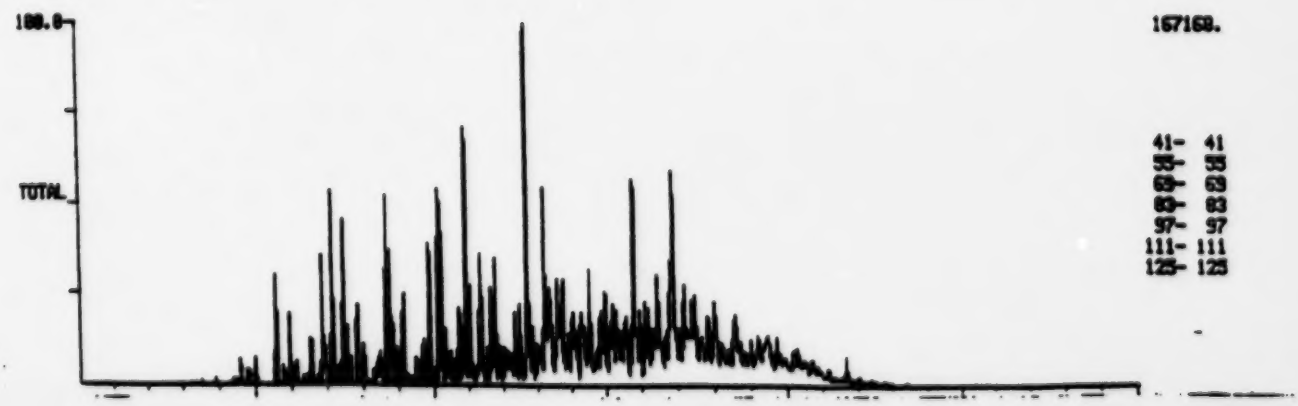
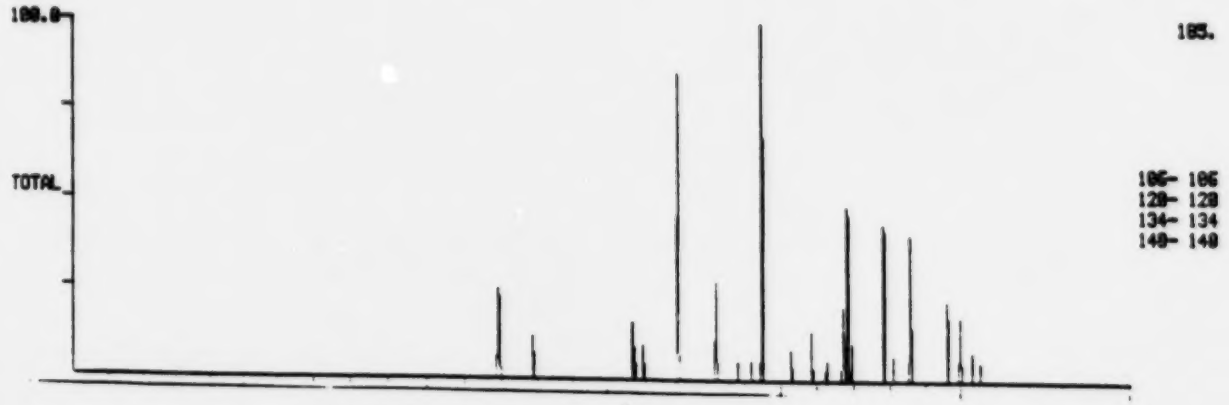


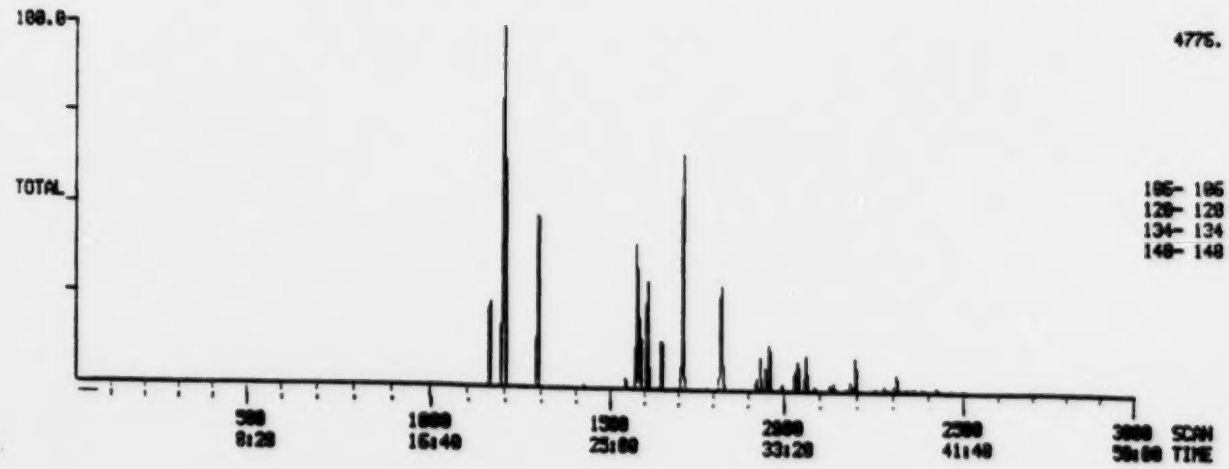
Figure 5(A)

The reconstructed ion chromatograms for the aromatic compounds found in the Naphtha Cut of the 1985 primary and fire flood production samples.

PRIMARY
P-1; 85/11

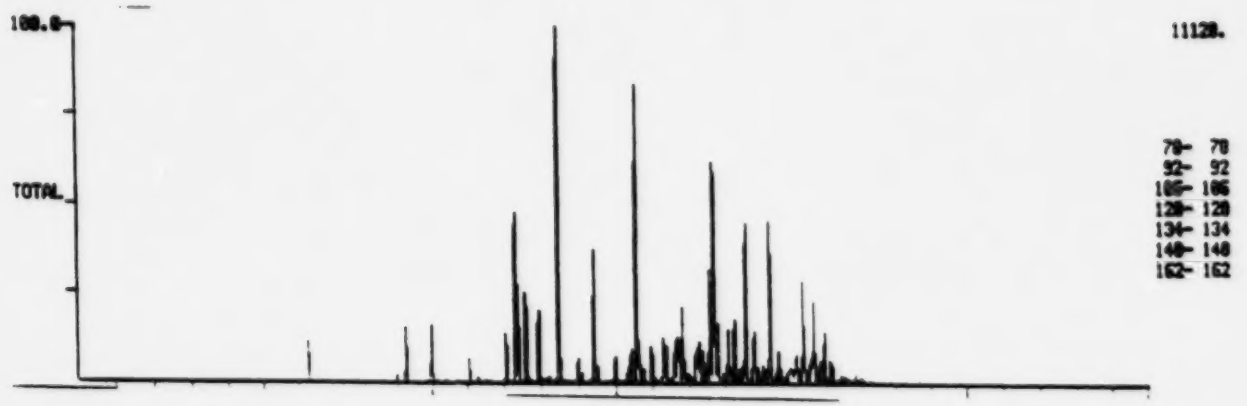


FIRE FLOOD
F-1; 85/11

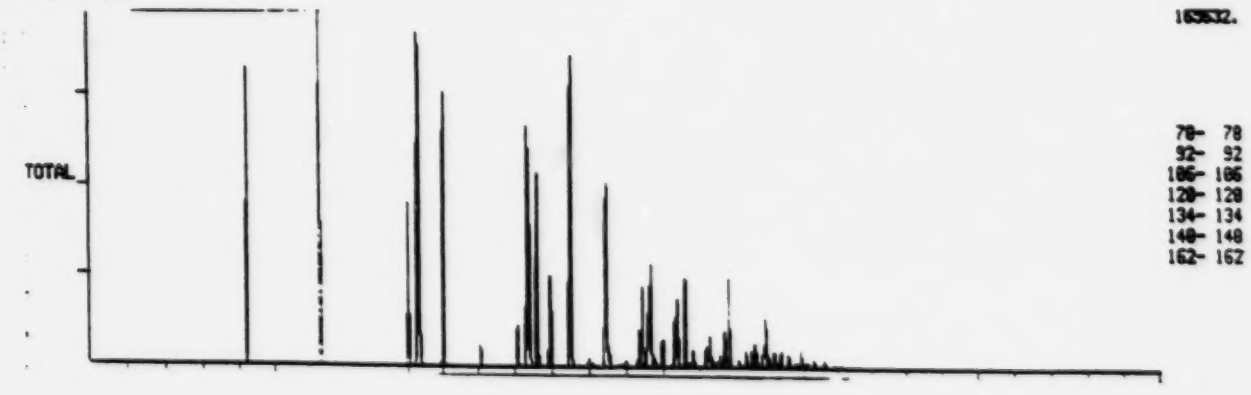


The reconstructed ion chromatogram for the aromatic compounds found in the Naphtha Cut of the 1987 primary and fire flood production samples.

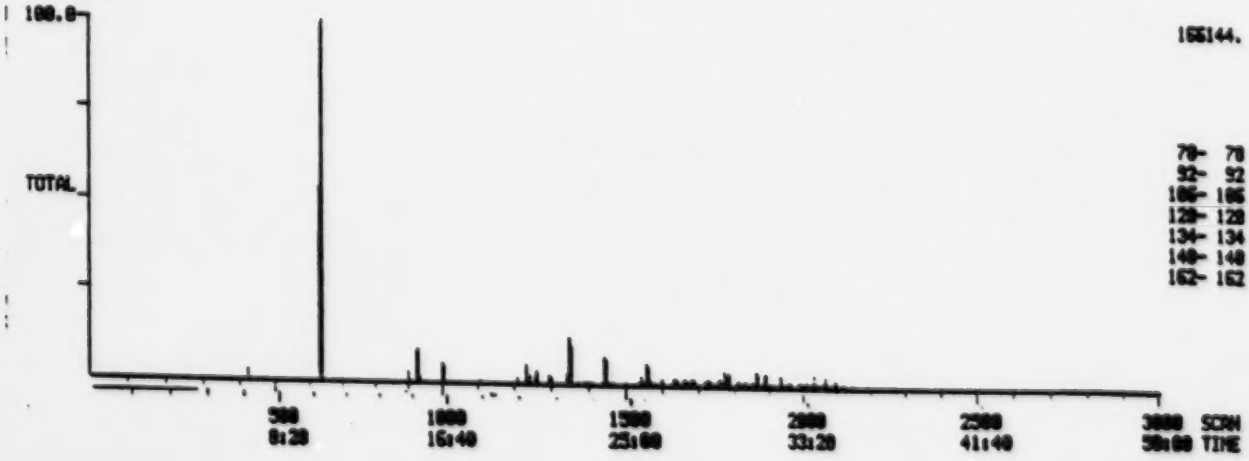
PRIMARY
P-1; 87/5



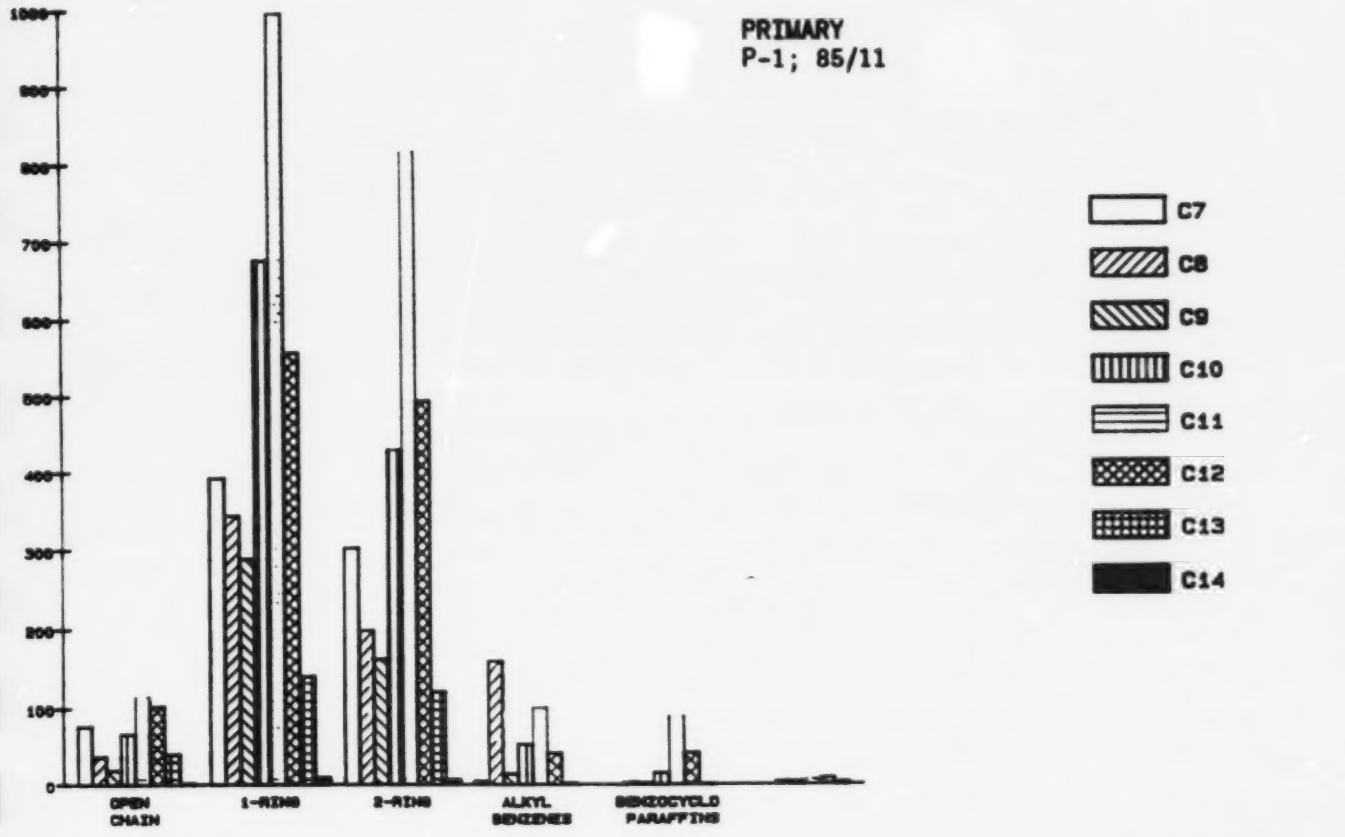
FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5



The distribution of compound types in the naphtha distillation cut of the primary and fire flood production samples for 1985.



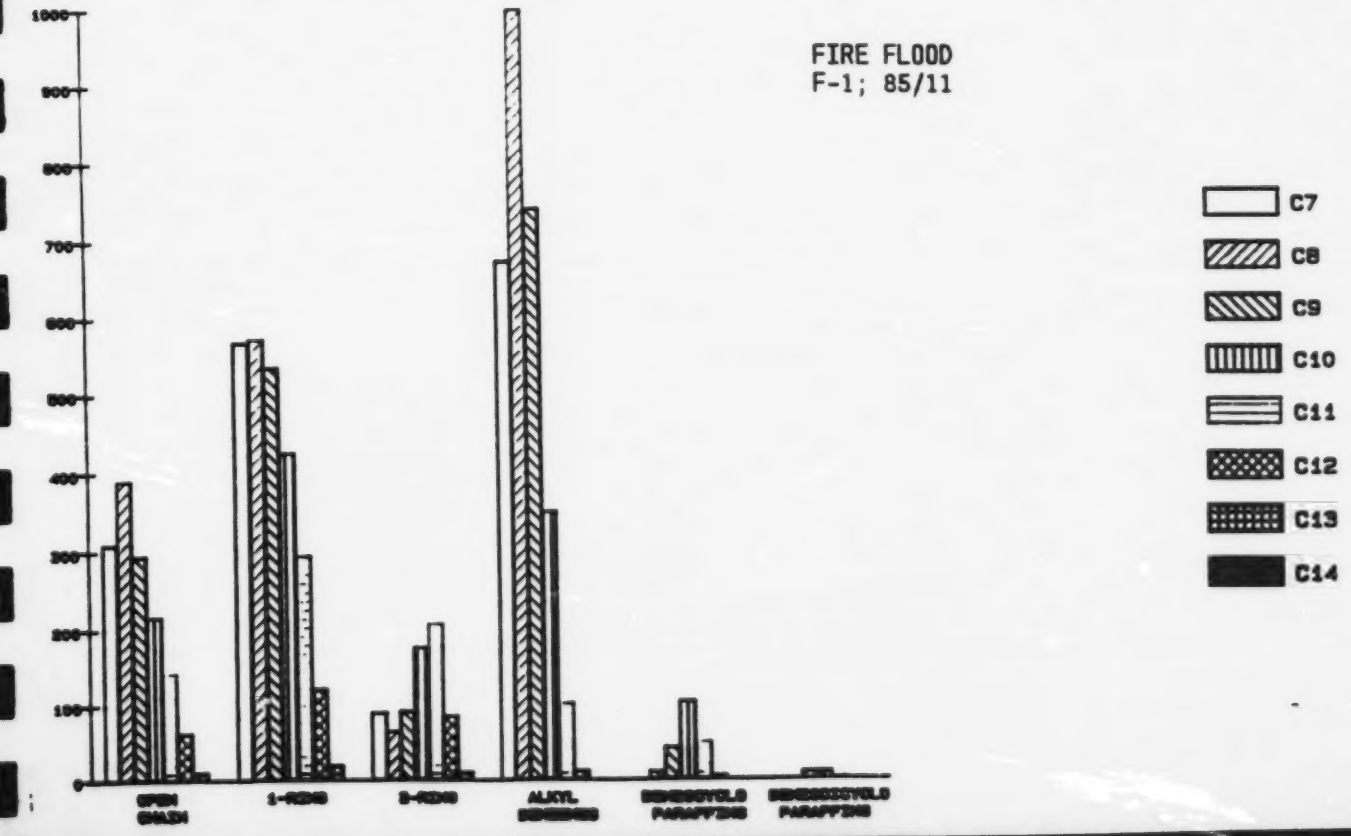


Figure 6(B)

The distribution of compound types in the naphtha distillation cut of the primary and fire flood production samples for 1987.

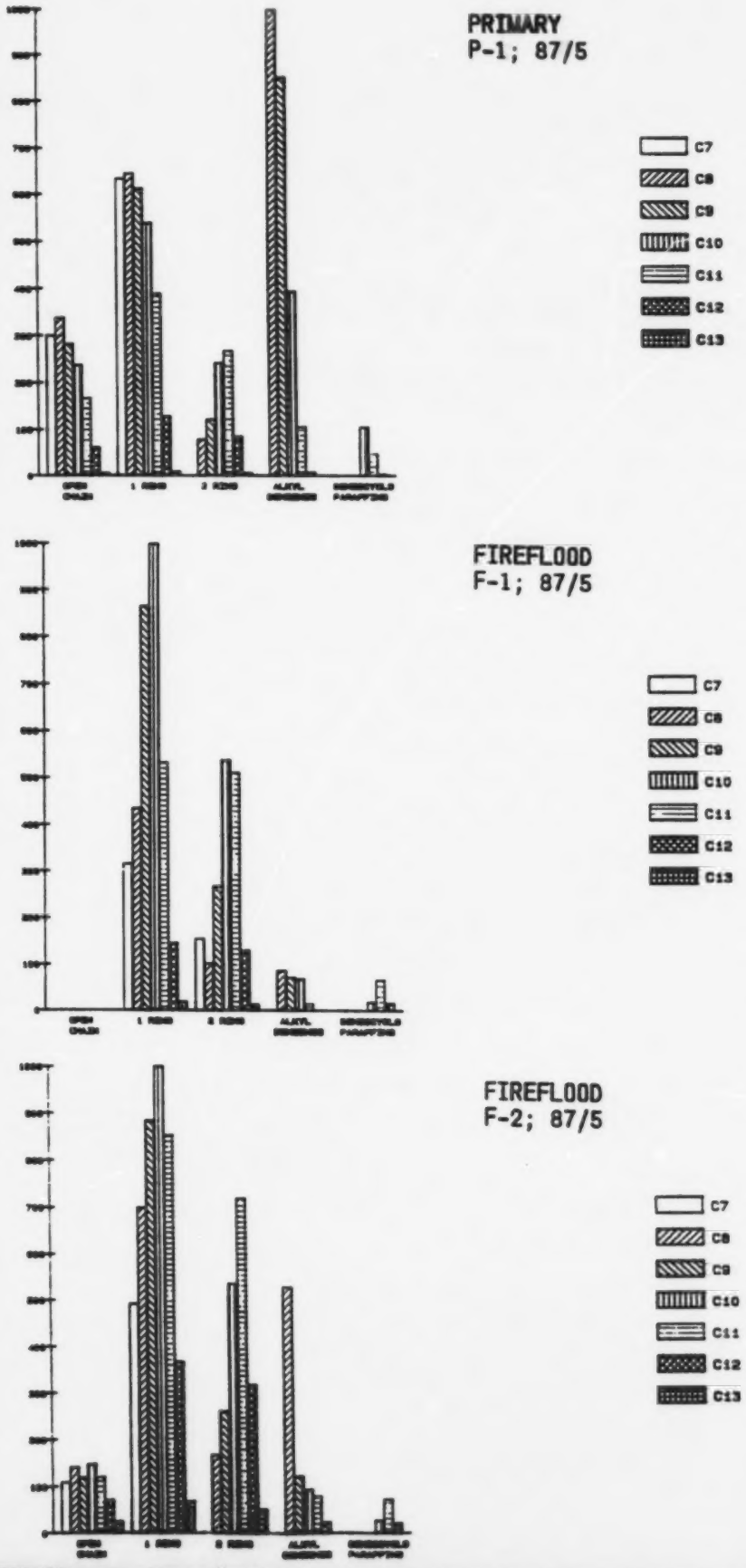


Figure 7(A)

The total ion chromatograms of the saturates fraction of the middle distillate from the 1985 primary and fire flood production under nitrous oxide chemical ionization.

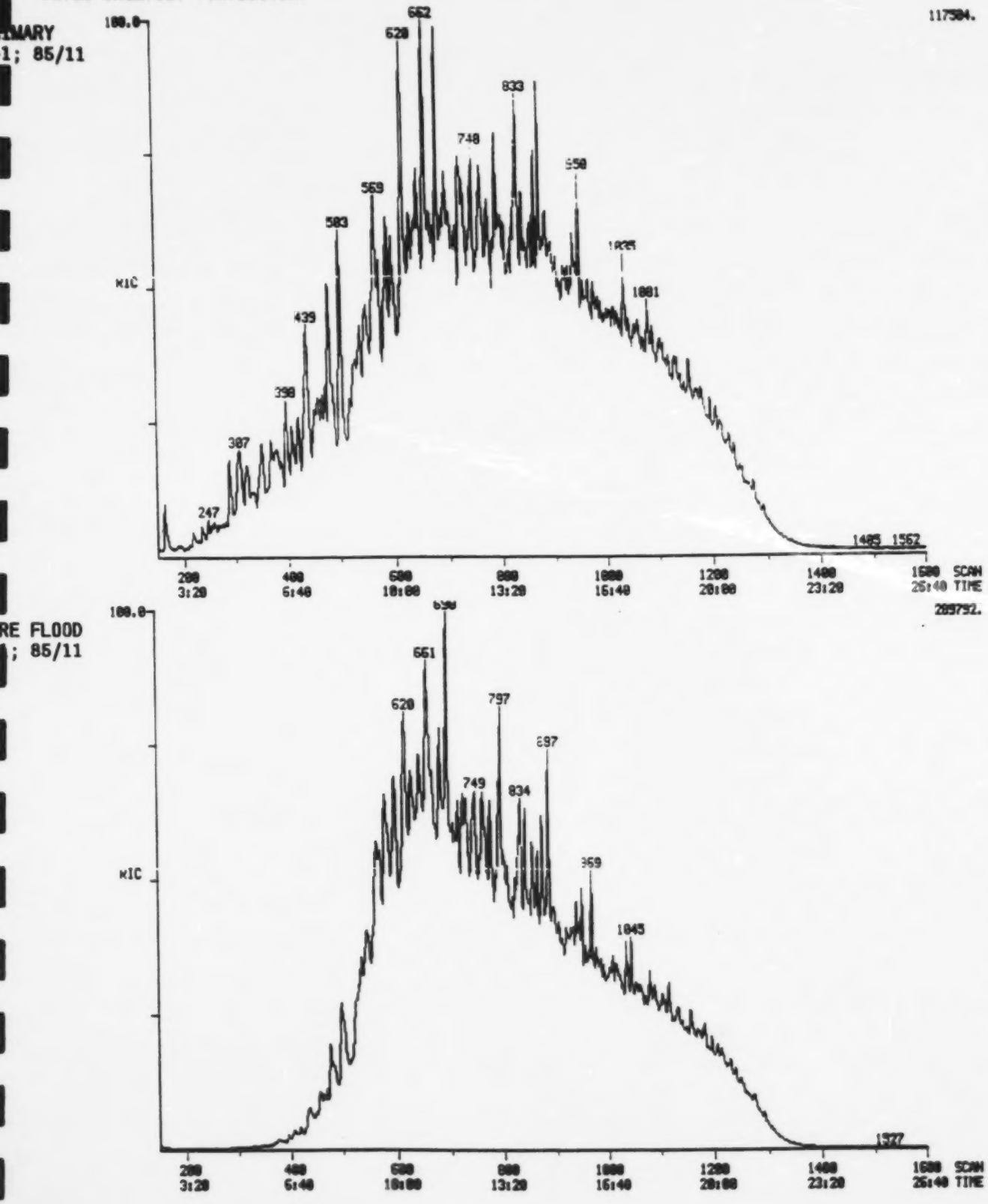
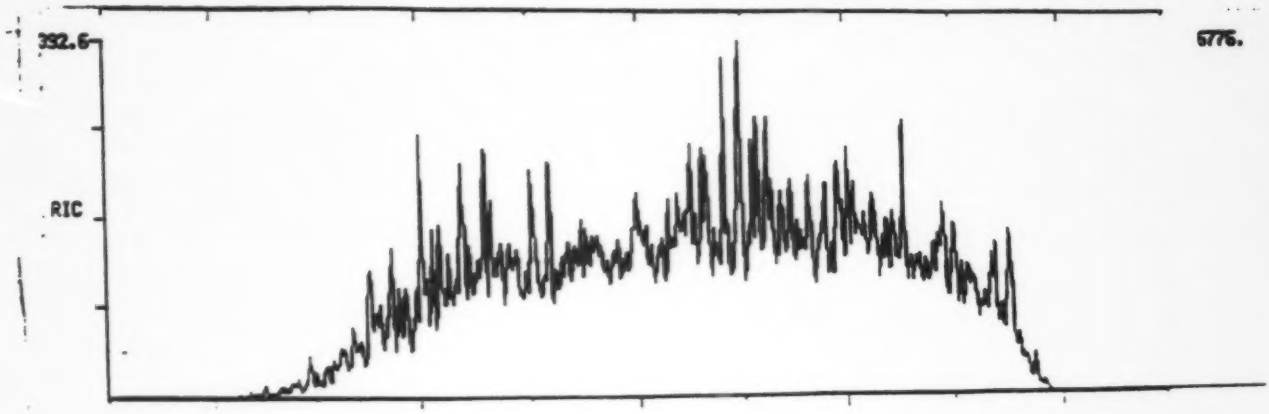


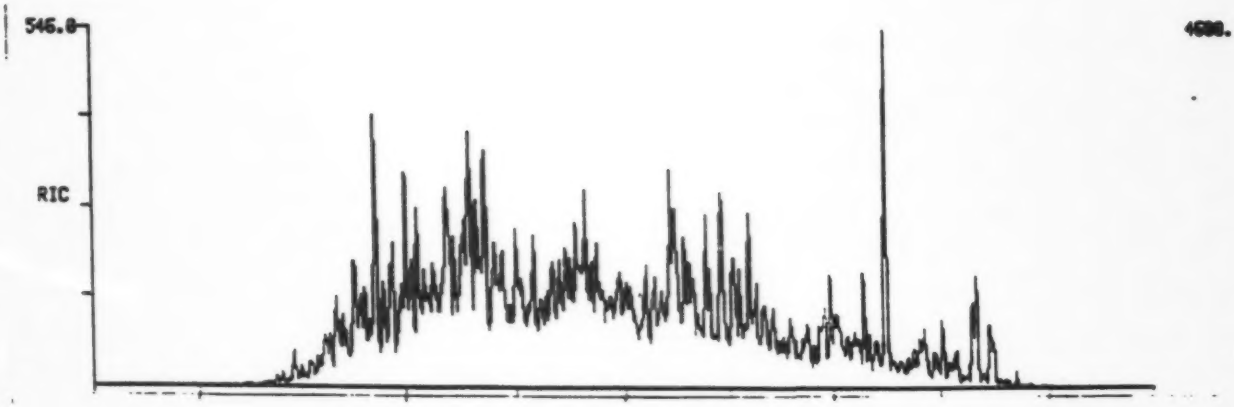
Figure 7(b)

The total ion chromatograms of the saturates fraction of the middle distillate from the 1987 primary and fire flood production under chemical ionization.

PRIMARY
P-1; 87/5



FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5

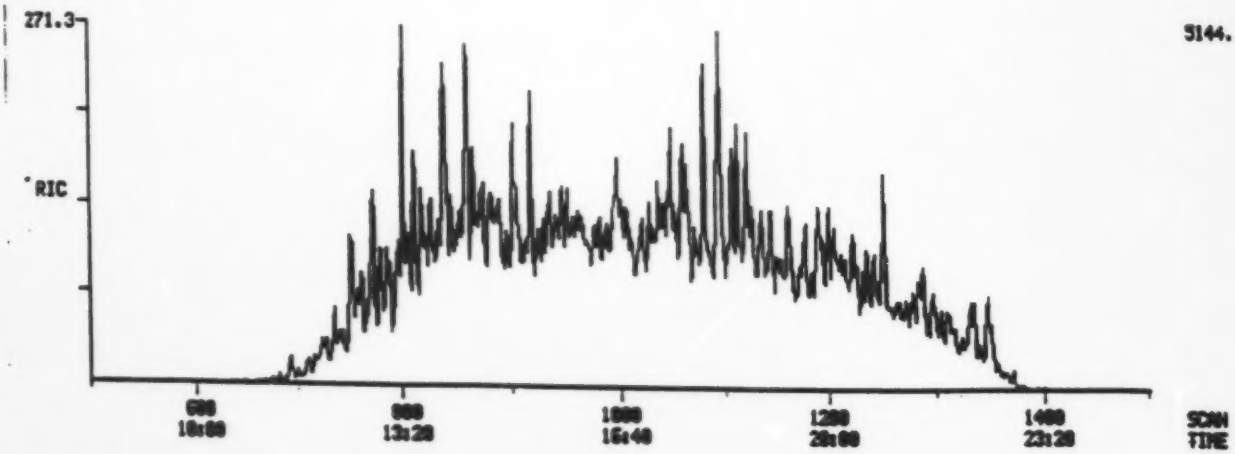
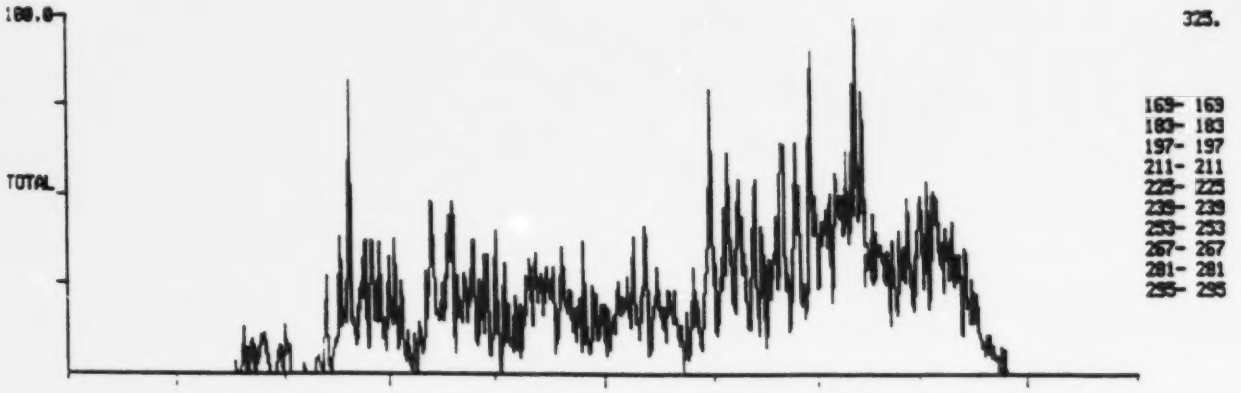


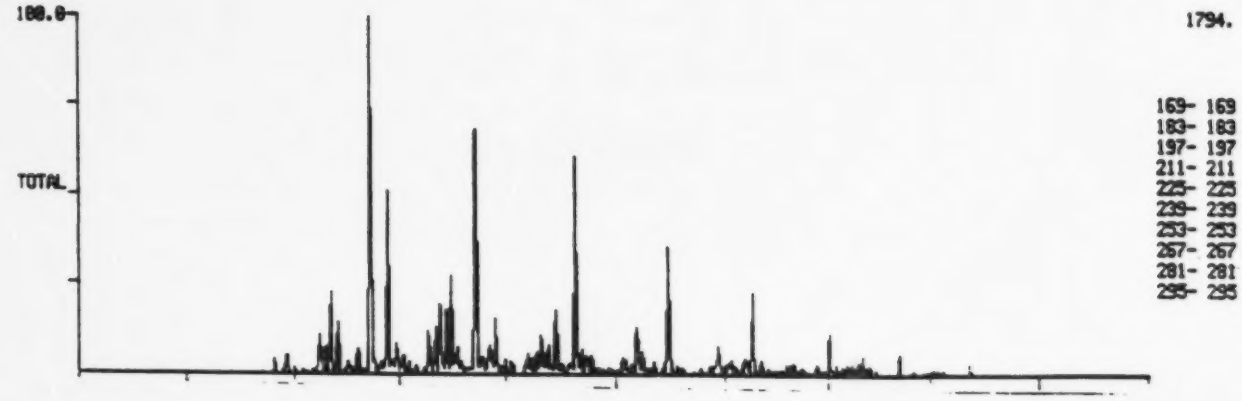
Figure 8

The reconstructed ion chromatograms for the open chain saturates of the saturates fraction of the middle distillate from the primary production.

PRIMARY
P-1; 87/5



FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5

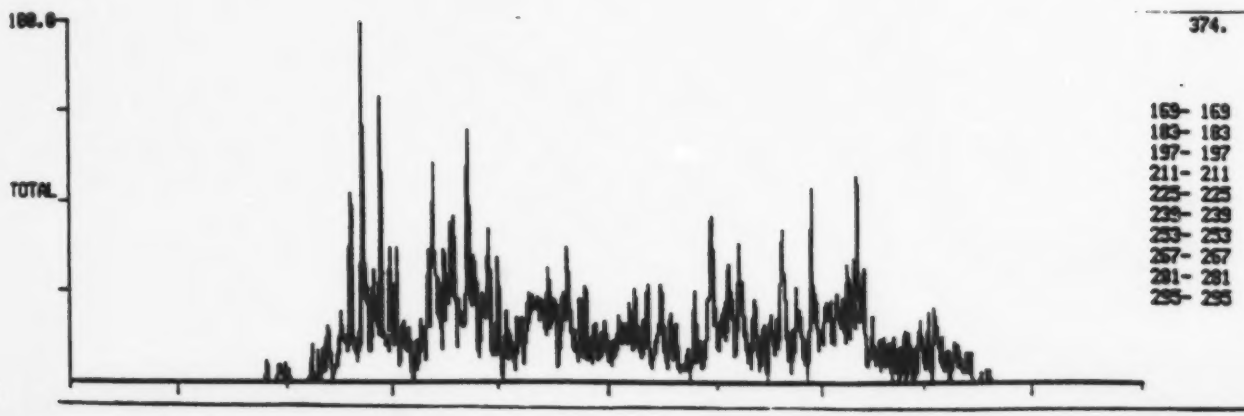
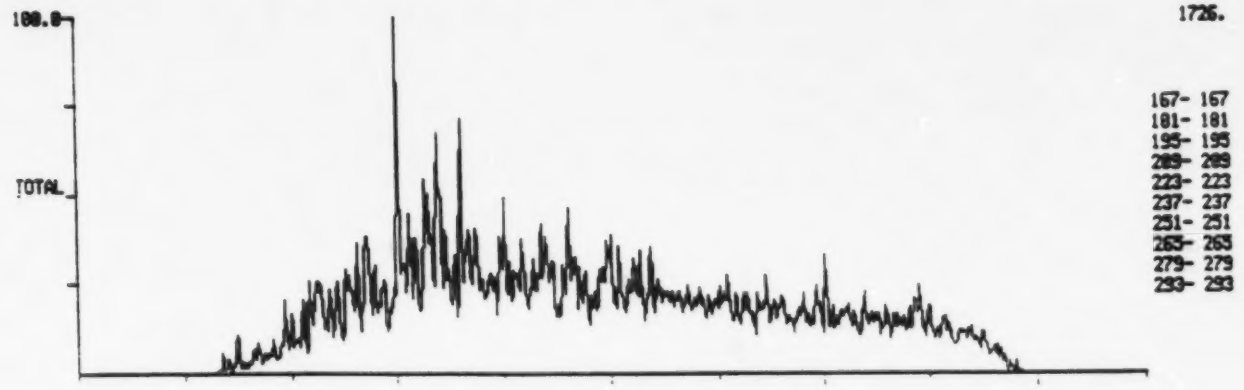


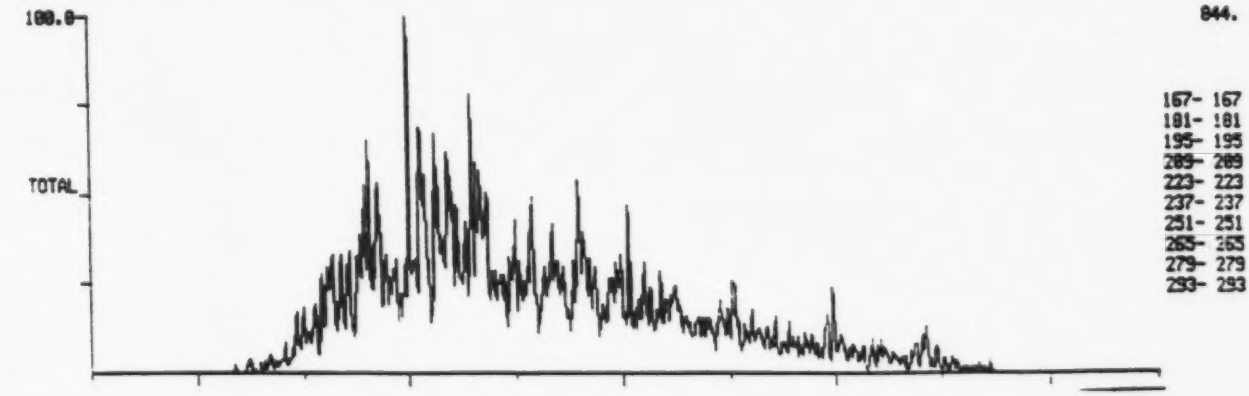
Figure 5

The reconstructed ion chromatograms of the one ring saturate compounds in the saturates fraction of the middle distillate cut of the primary and fire flood production samples.

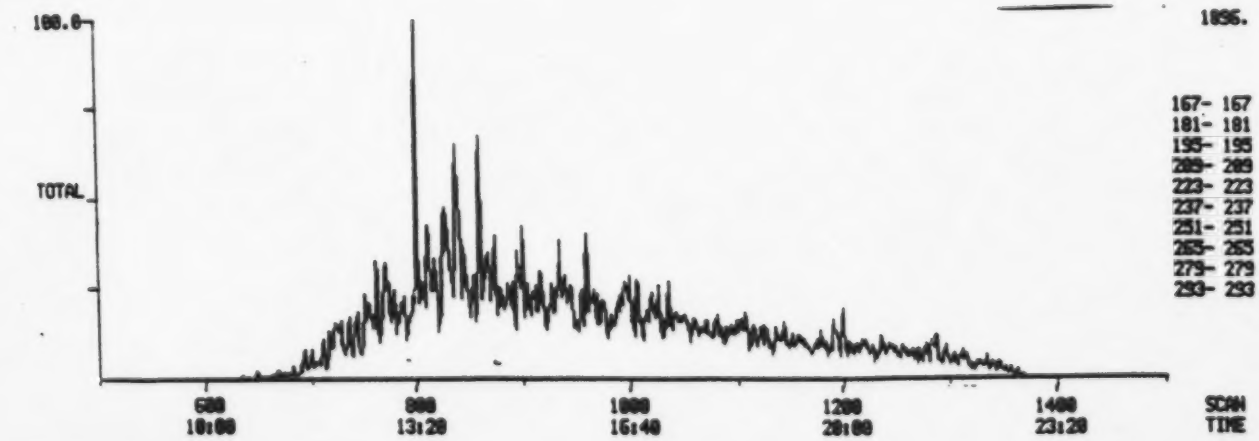
PRIMARY
P-1; 87/5



FIREFLOOD
F-1; 87/5

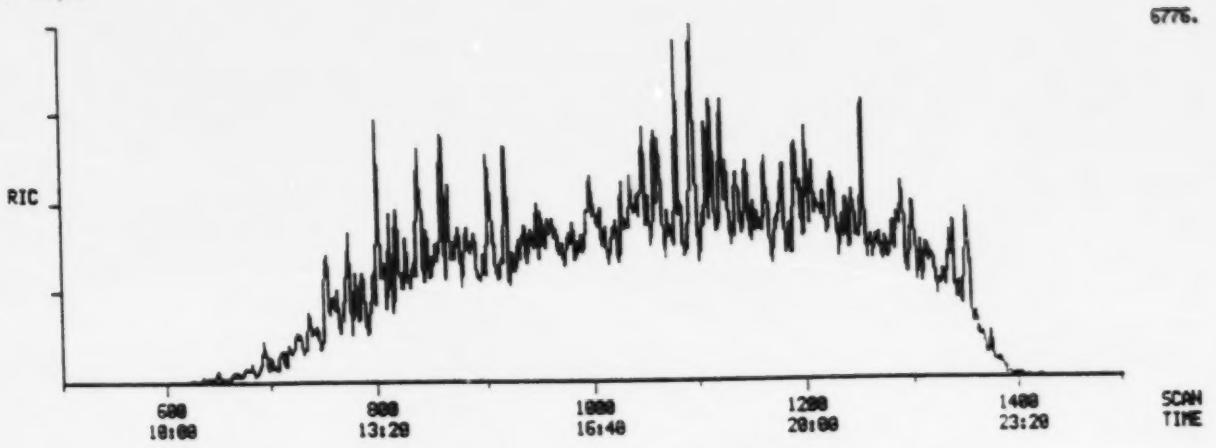


FIREFLOOD
F-2; 87/5

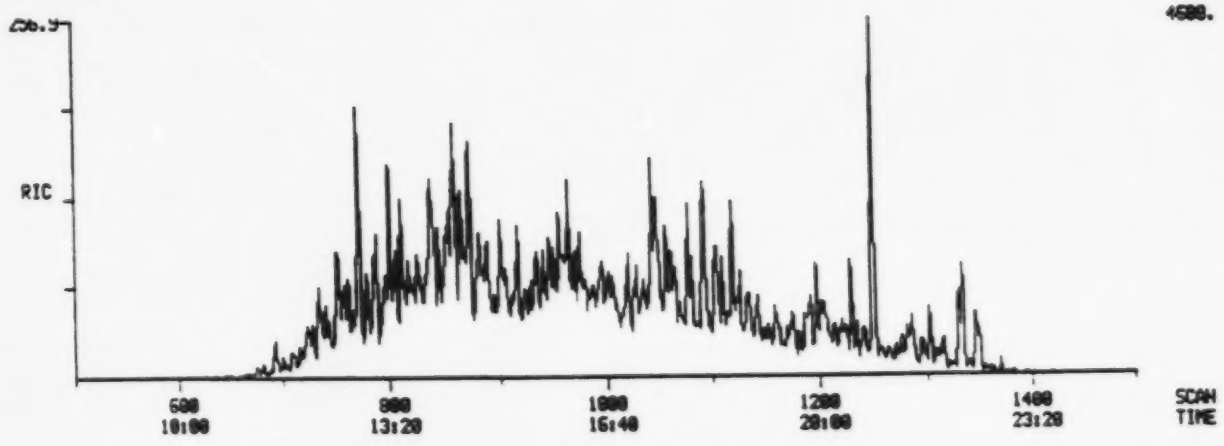


The reconstructed ion chromatograms of the 2-ring saturate compounds in the saturates fraction of the middle distillate cut for the primary and fire flood production samples.

PRIMARY
P-1; 87/5



FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5

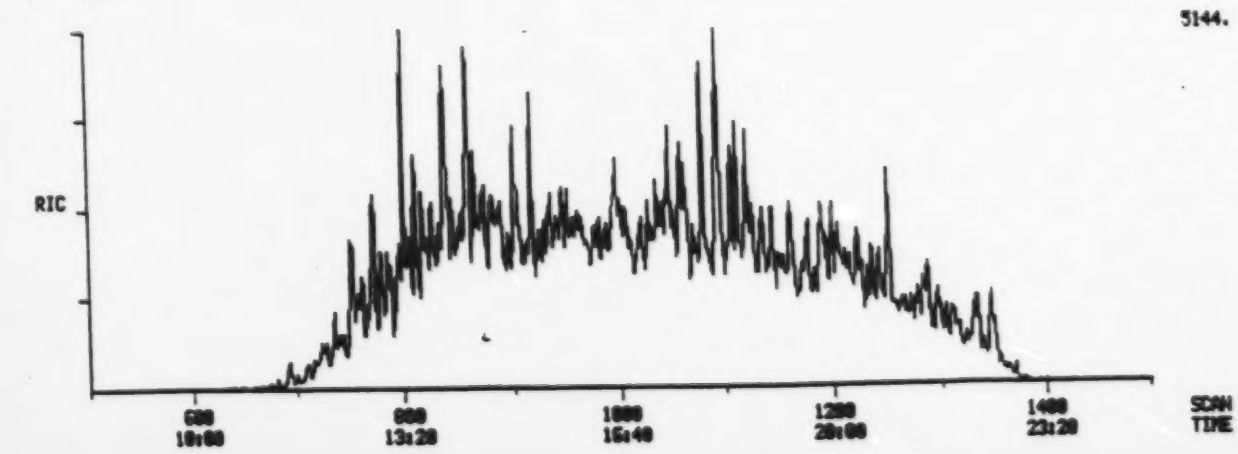
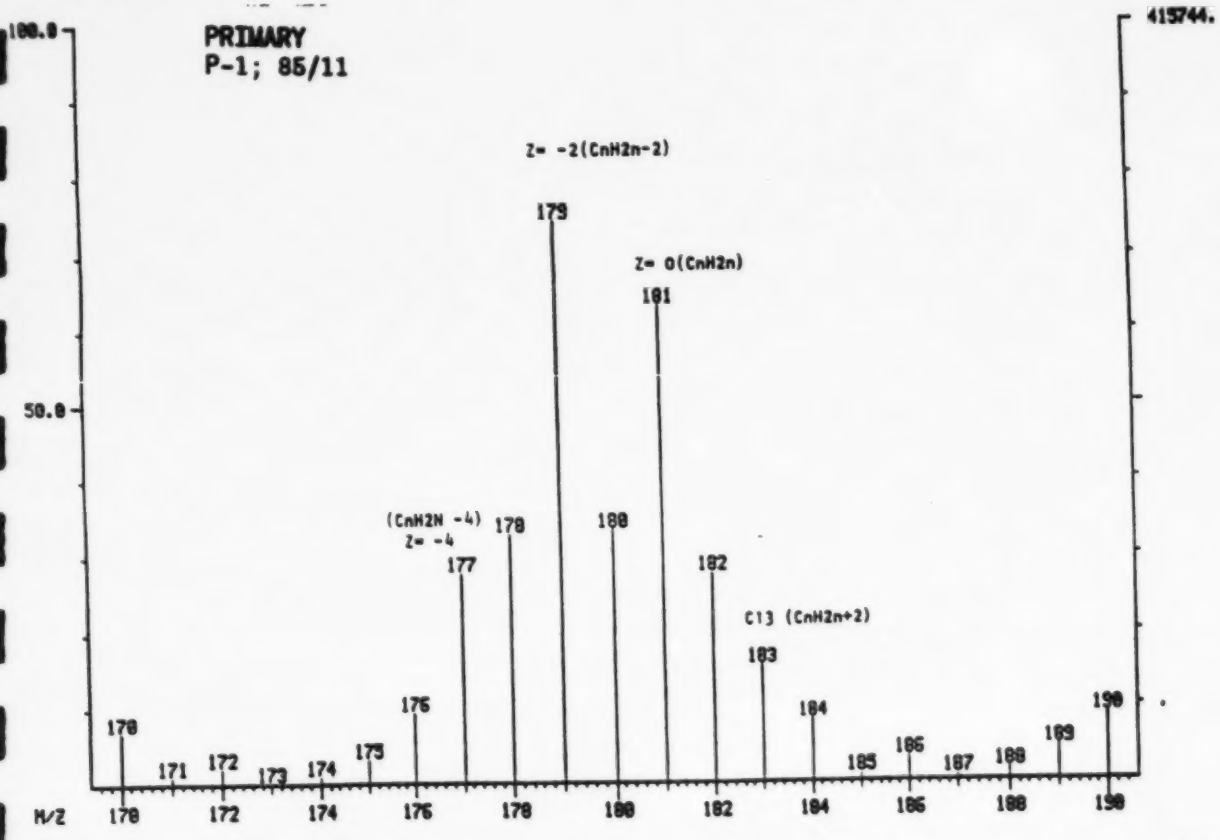


Figure 11

The summed mass spectrum of the saturates fraction of the middle distillate between mass 170 and 190 to show the relative distribution of molecular species.



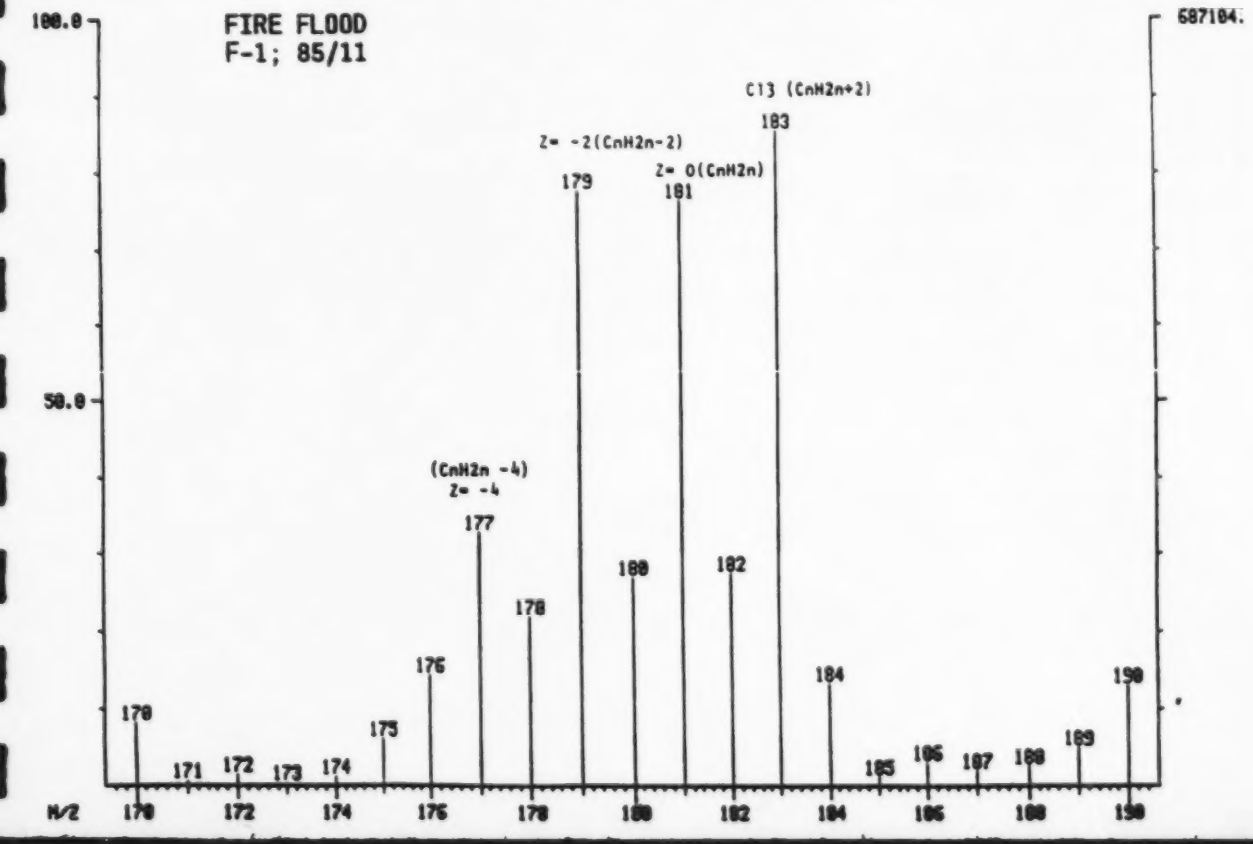


Figure 12(A) The distribution of compound types in the saturates fraction of the middle distillate cut of the 1985 primary and fire flood production samples.

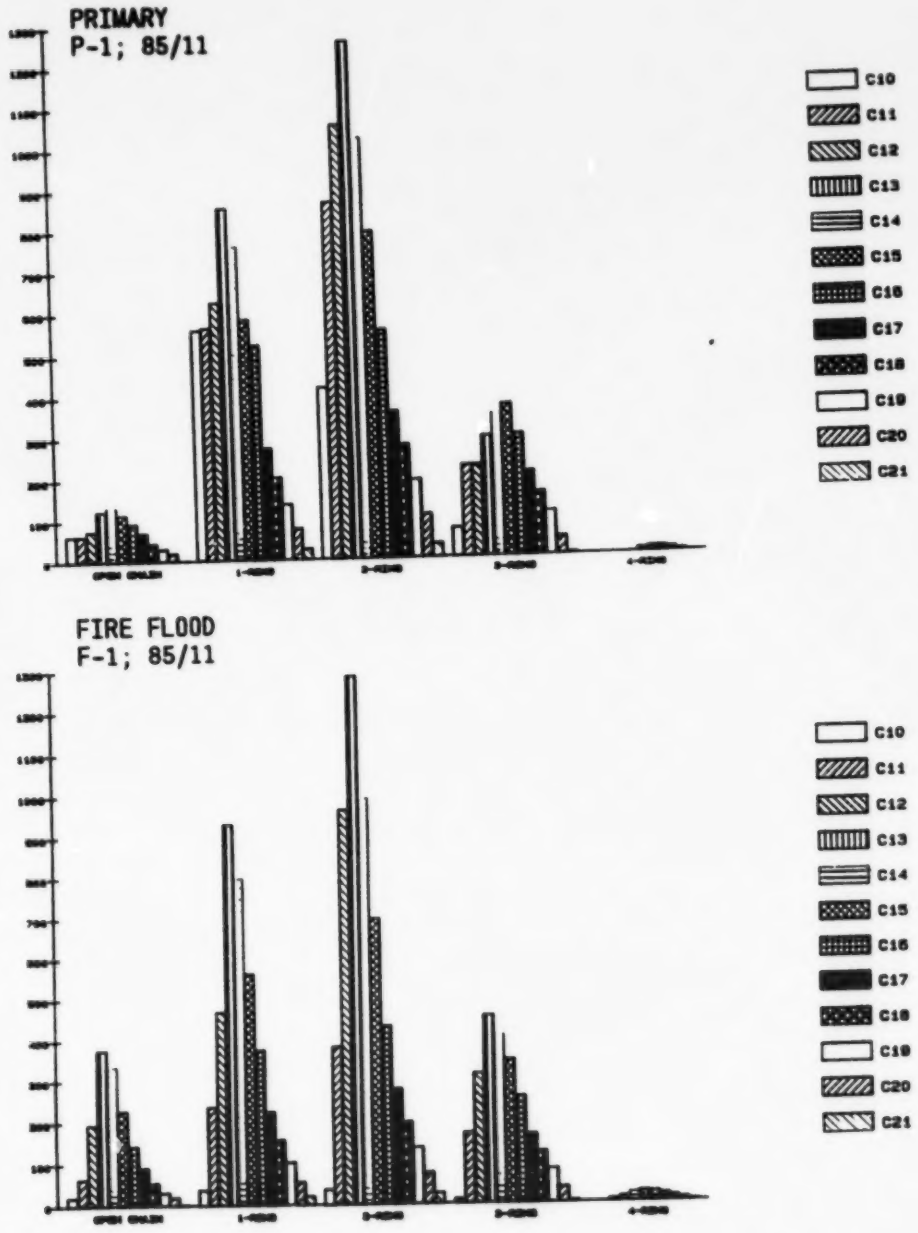


Figure 12(B) The distribution of compound types in the saturates fraction of the middle distillate cut of the 1987 primary and fire flood production samples.

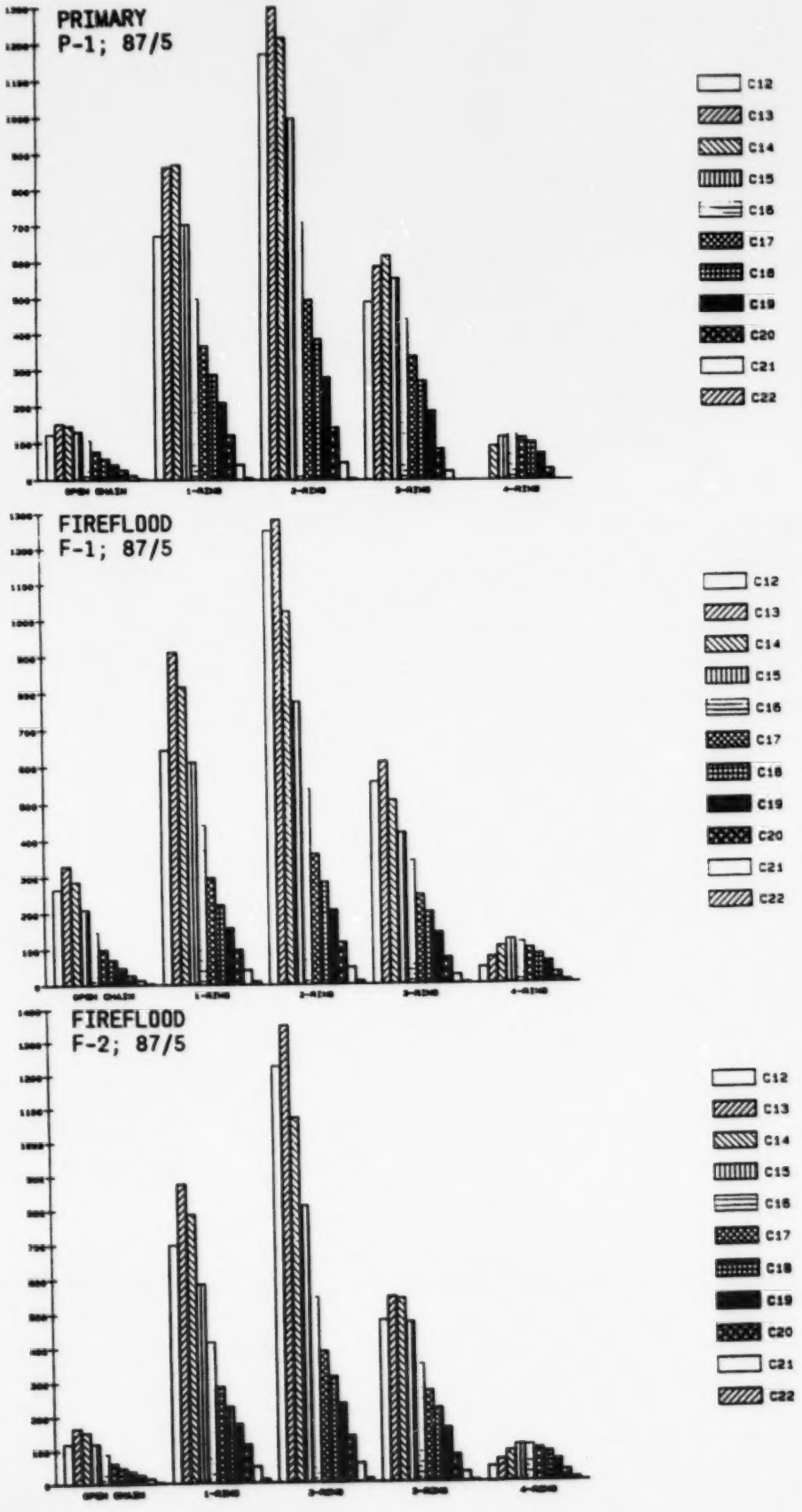


Figure 13(A)

The total ion chromatograms of the aromatics fraction of the middle distillate from the 1985 primary and fire flood production samples.

PRIMARY
P-1; 85/11

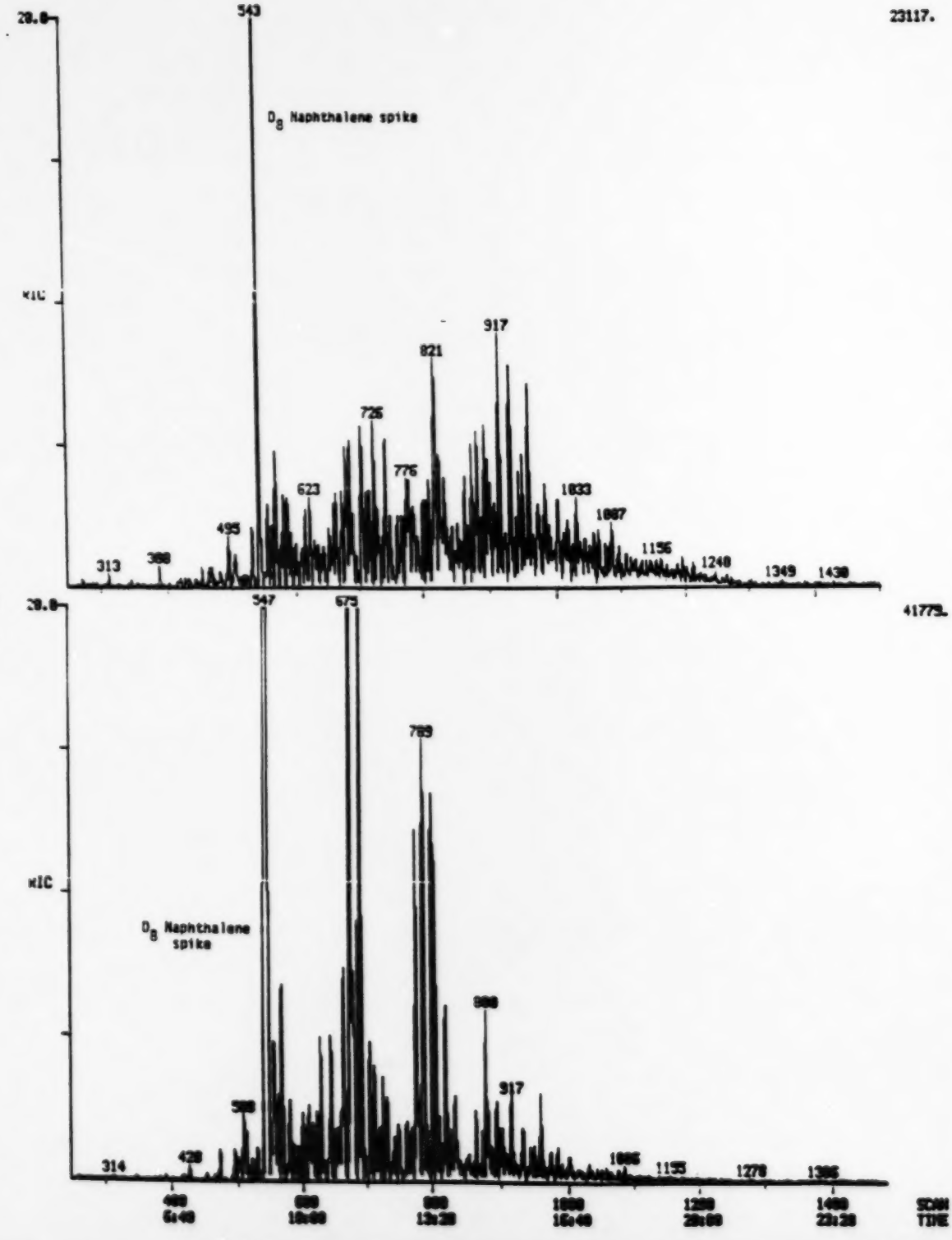


Figure 13(B)

The total ion chromatograms of the aromatics fraction of the middle distillate from the 1985 primary and fire flood production samples.

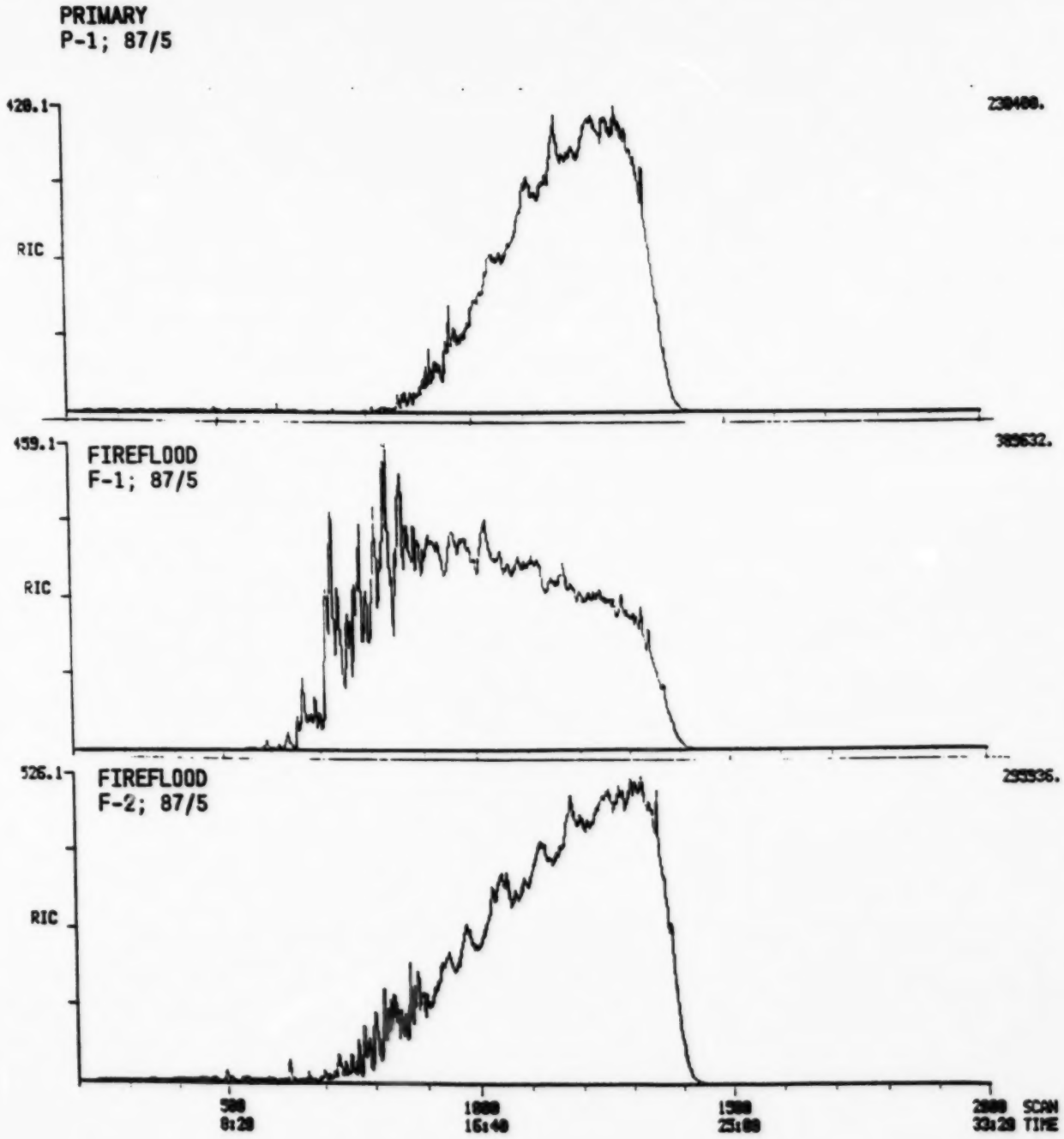


Figure 14

The reconstructed ion chromatograms of the alkyl benzenes in the aromatics fraction of the middle distillate cut from the 1987 primary and fire flood production sample.

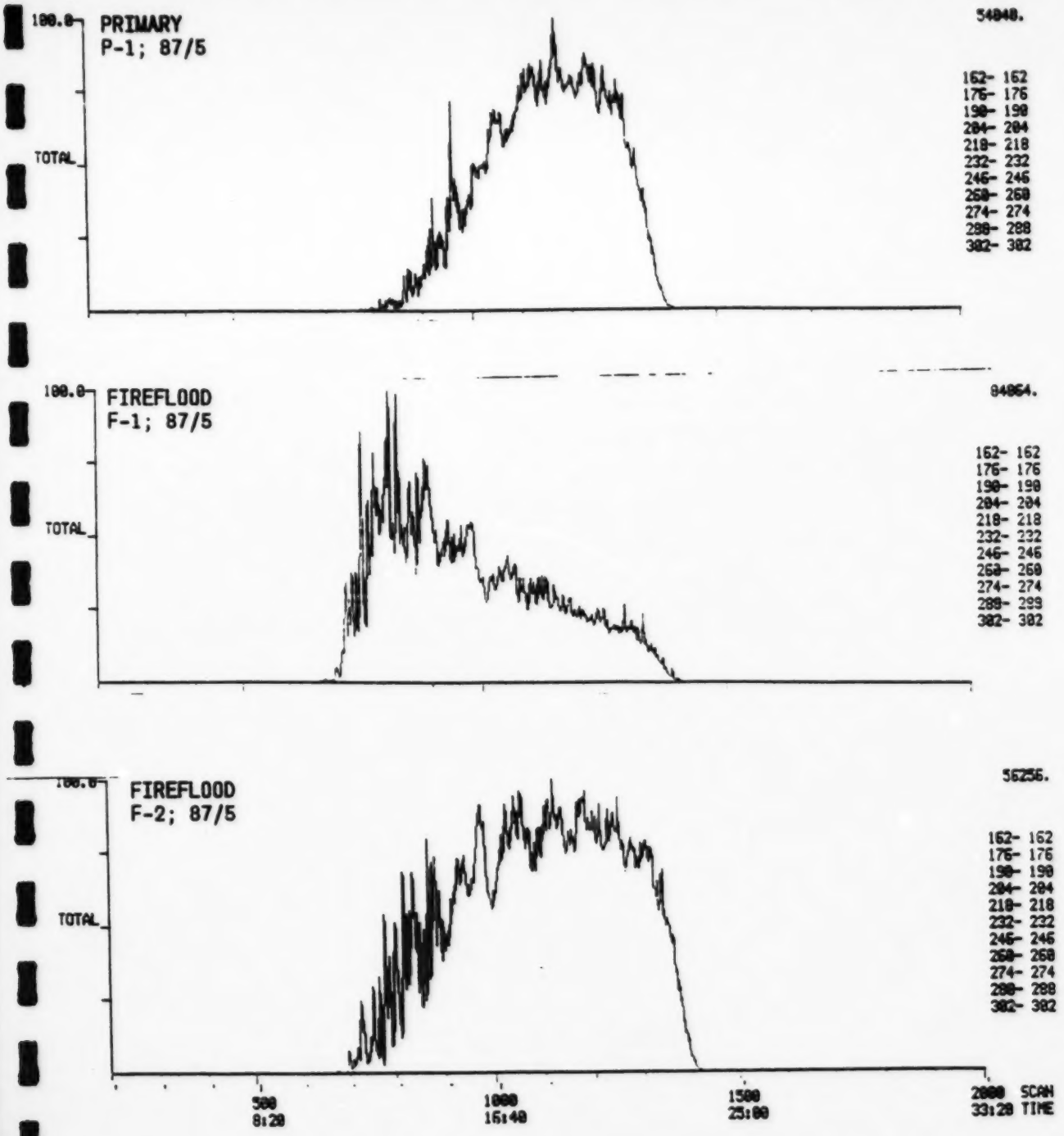


Figure 15

The reconstructed ion chromatograms of the benzocyclo paraffins in the aromatics fraction of the middle distillate from 1987 primary and fire flood production samples.

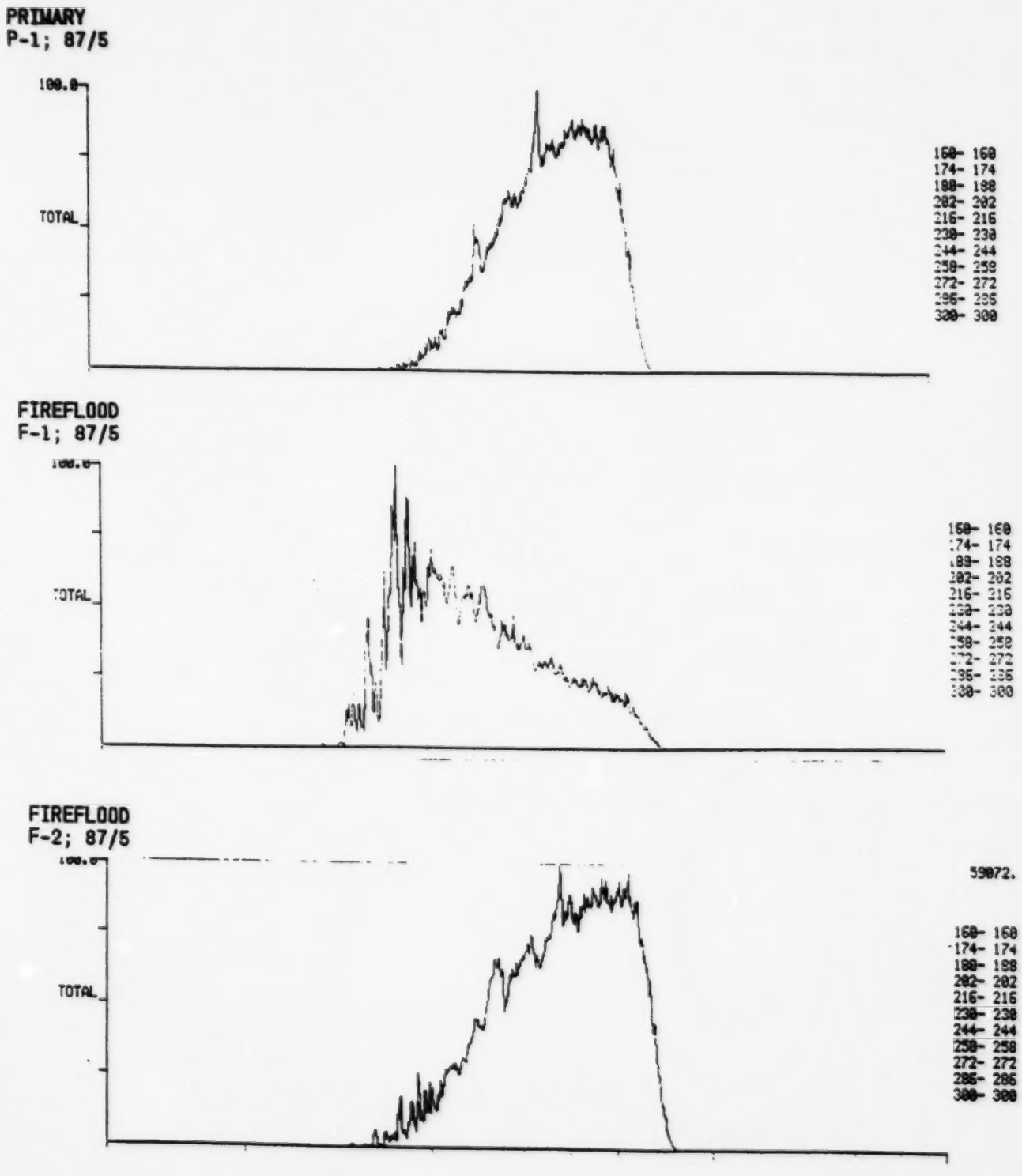


Figure 16

The reconstructed ion chromatograms of the benzodicyclo paraffins in the aromatics fraction of the middle distillate from 1987 primary and fire flood production samples.

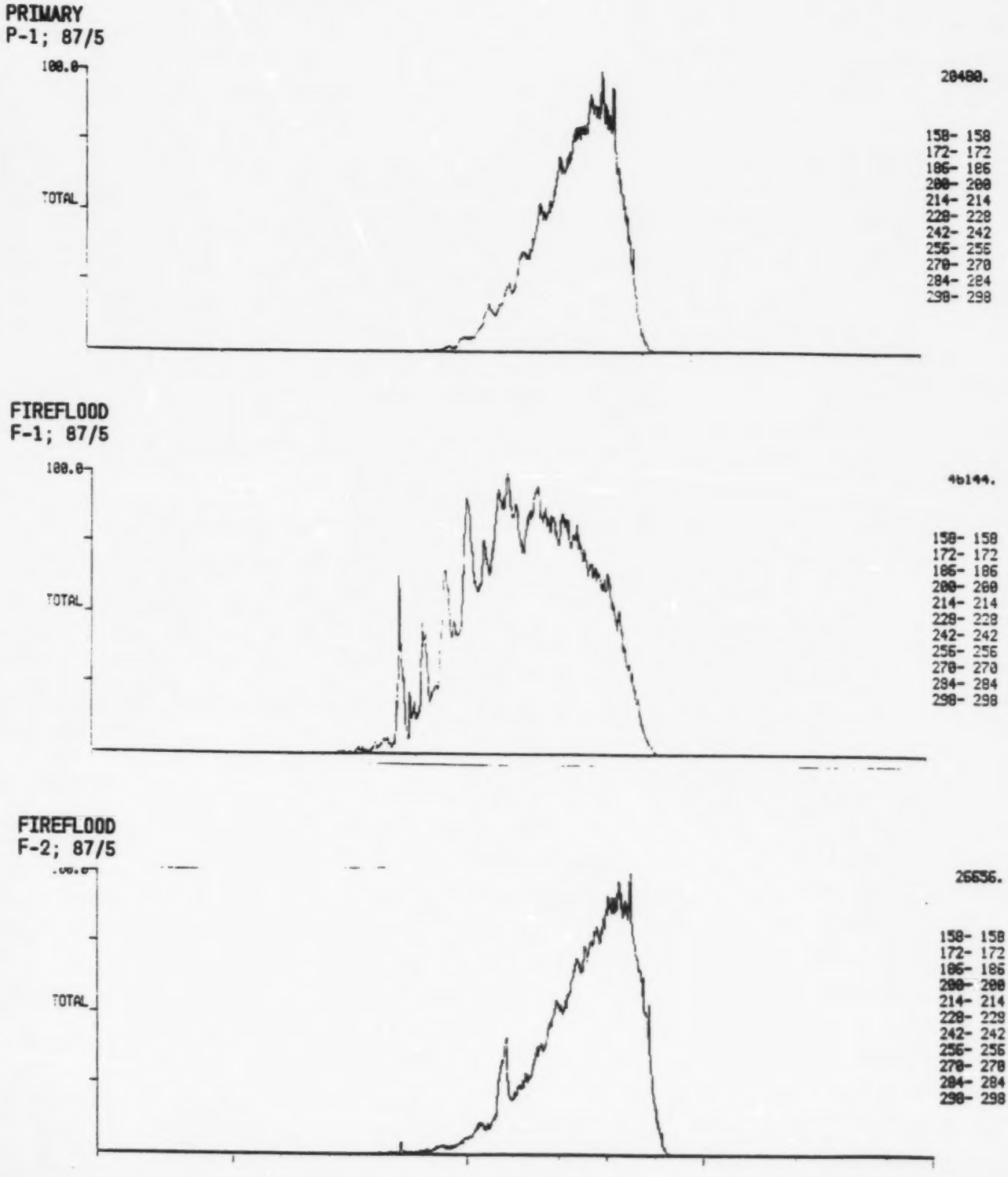


Figure 17

The reconstructed ion chromatograms of the Fluorenes/Anthracenes in the aromatics fraction of the middle distillate from 1987 primary and fire flood production samples.

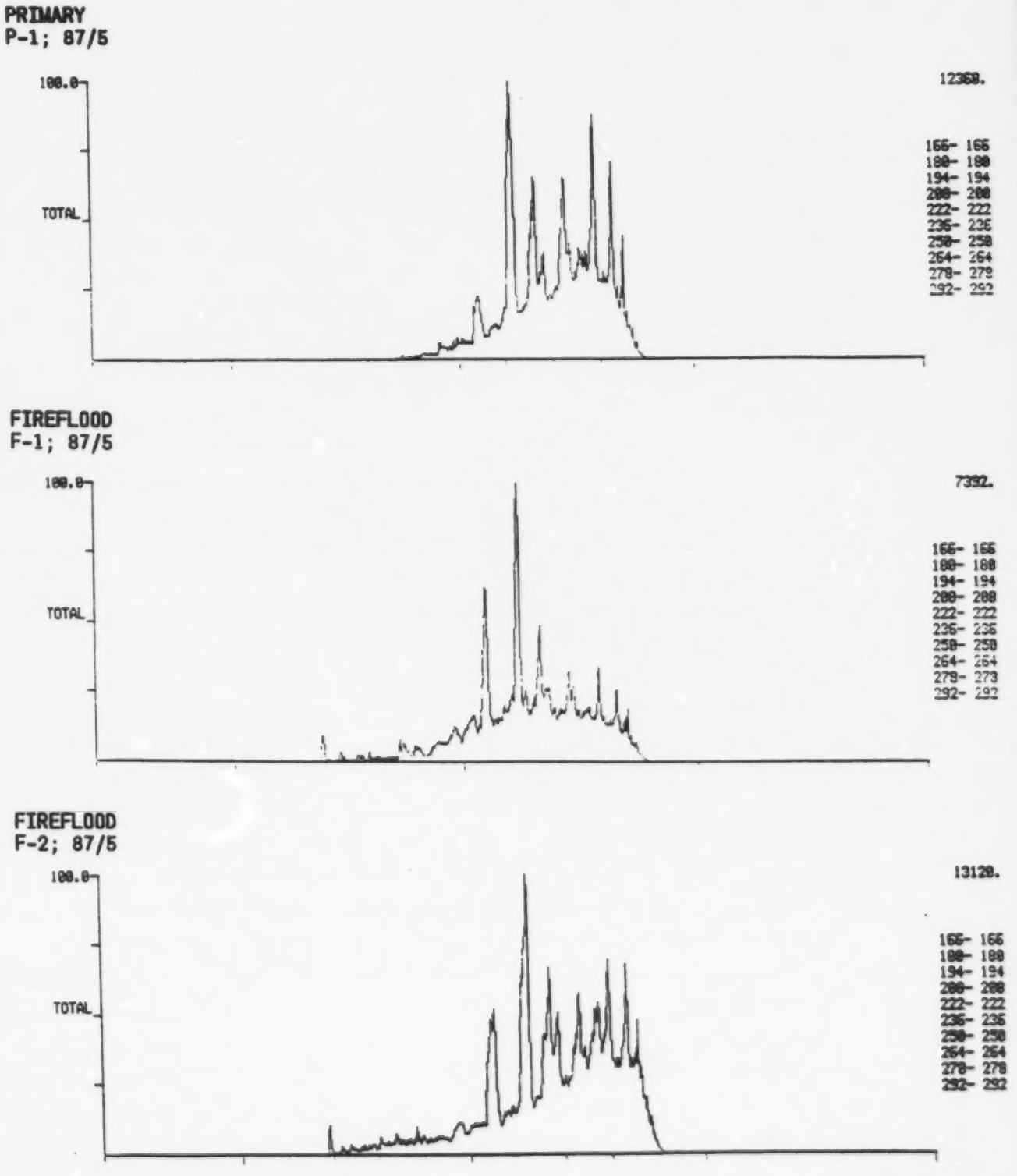
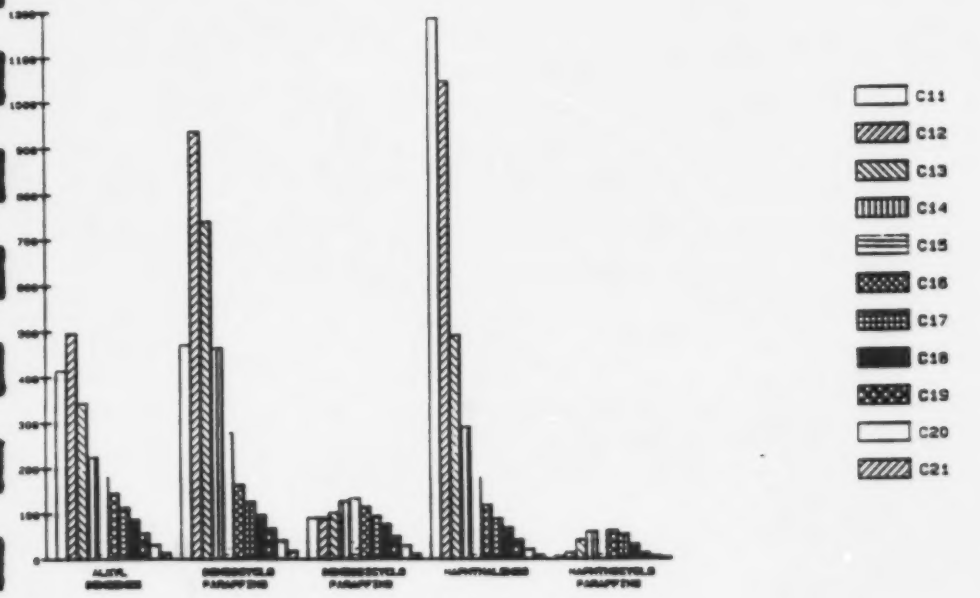


Figure 18(A)

The distribution of compound types in the aromatics fraction of the middle distillate cut in the 1985 primary and fire flood production samples.

PRIMARY
P-1; 85/11



FIRE FLOOD
F-1; 85/11

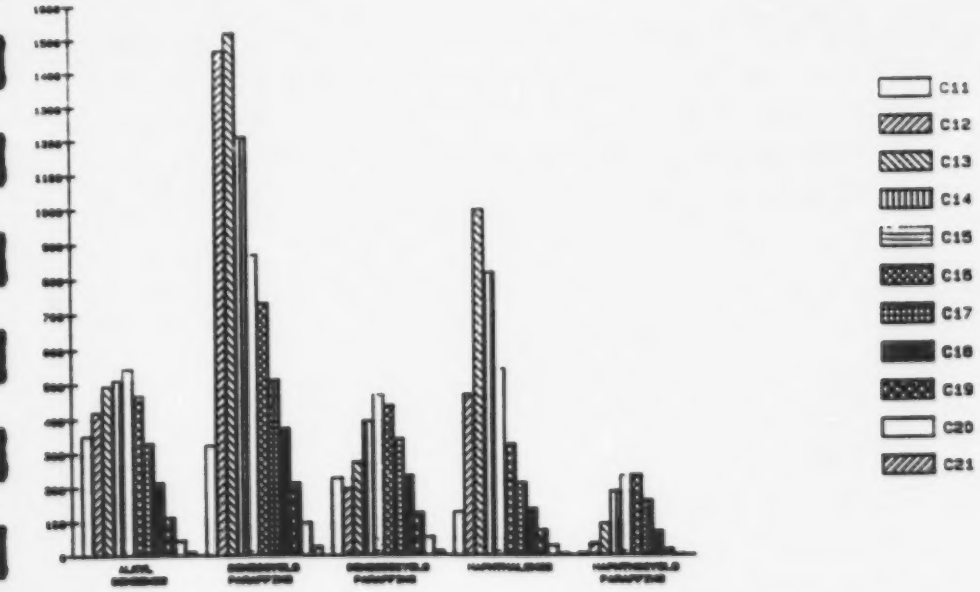


Figure 20(a)

The distribution of compound types in the aromatics fraction of the middle distillate cut in the 1987 primary and fire flood production samples.

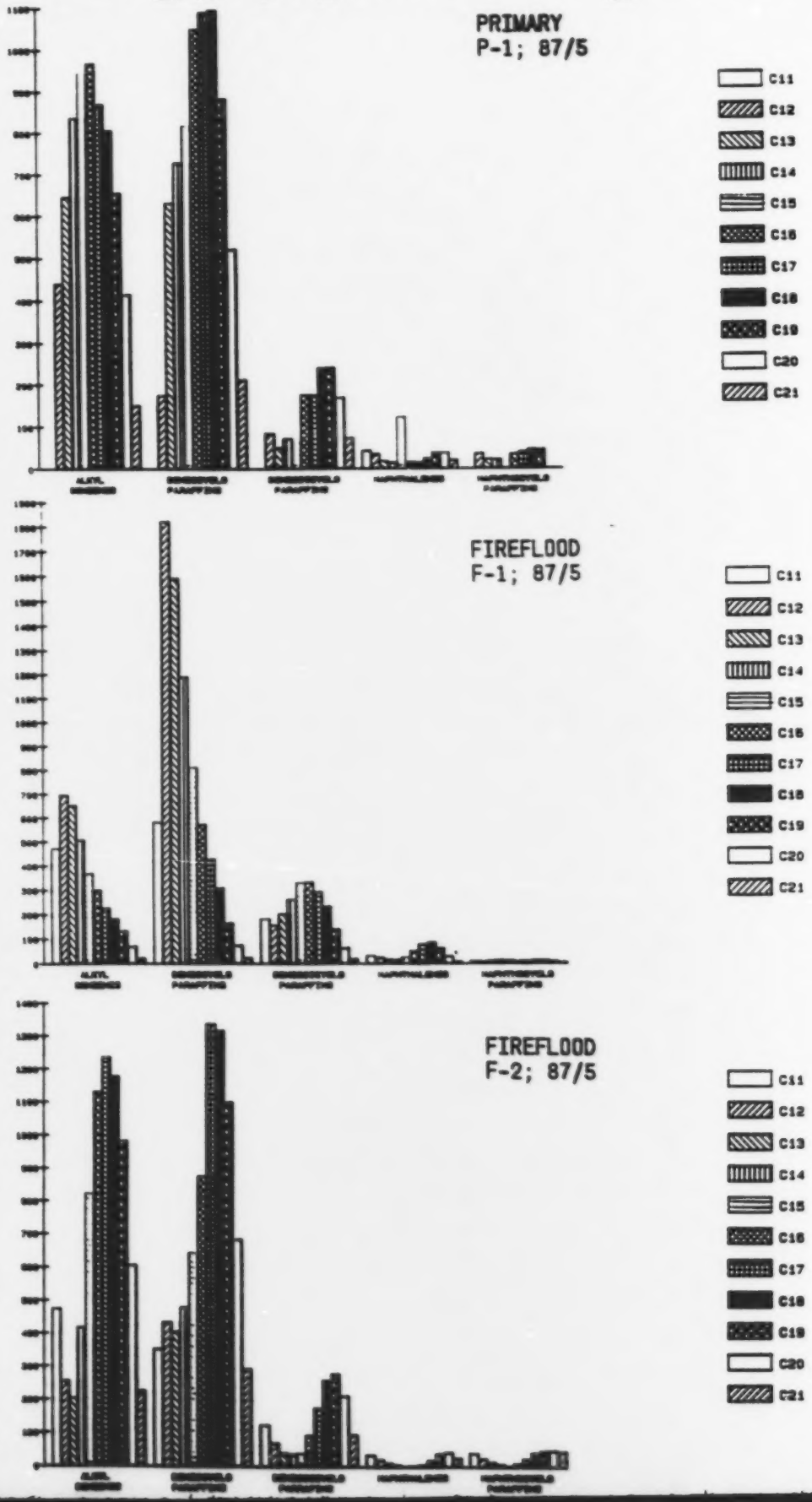


Figure 19(A)

The total ion chromatograms of the chromatographic fraction 3 of the middle distillate cut from the 1985 primary and fire flood production samples.

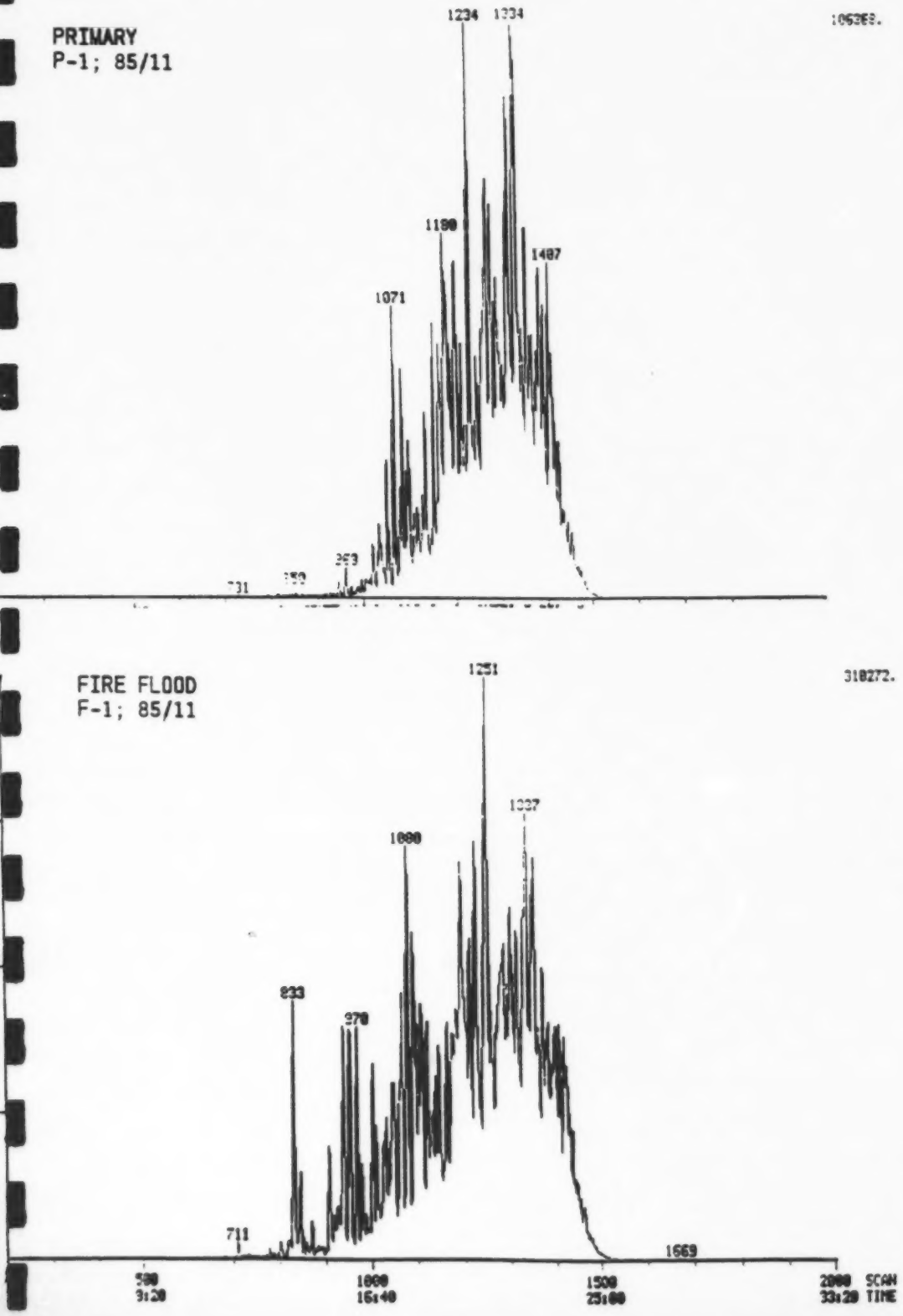


Figure 19(B)

The total ion chromatograms of the chromatographic fraction 3 of the middle distillate cut from the 1987 primary and fire flood production samples.

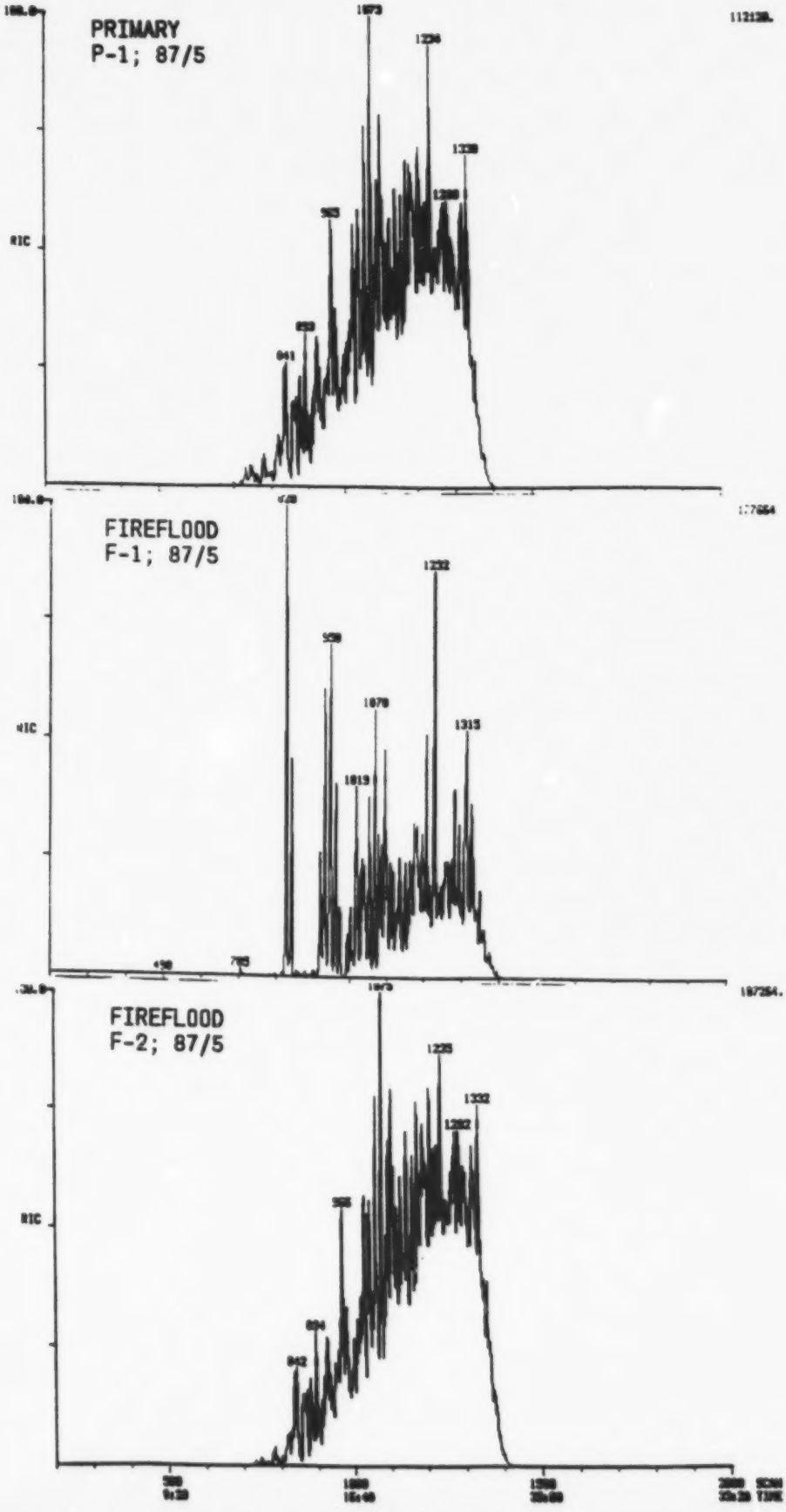
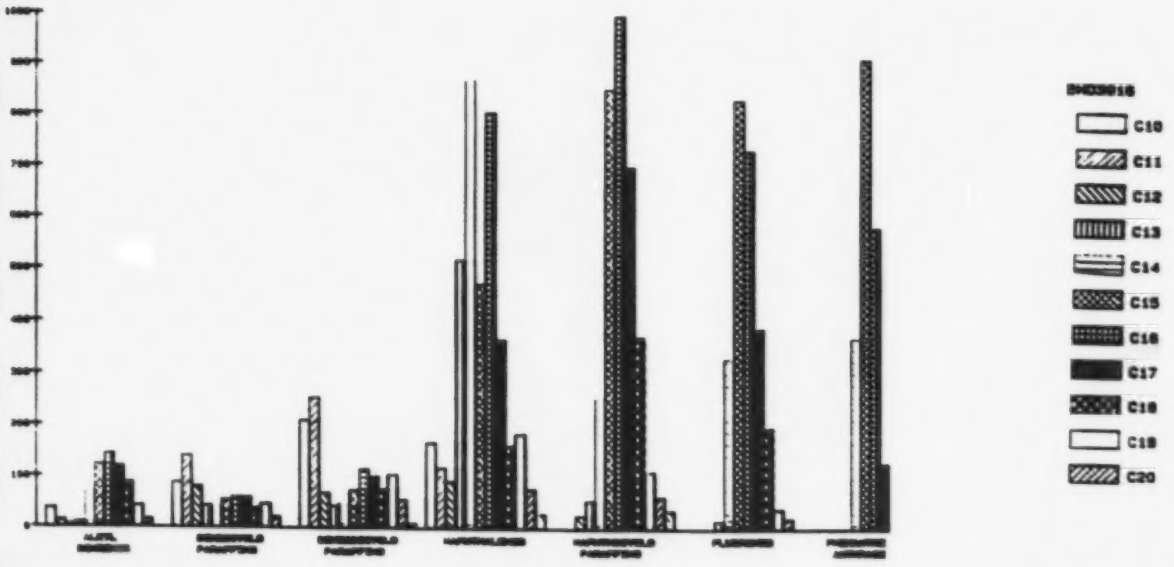


Figure 20(A)

The distribution of compound types in fraction 3 of the middle distillate cut in the 1985 primary and fire flood production samples.

PRIMARY
P-1; 85/11



FIRE FLOOD
F-1; 85/11

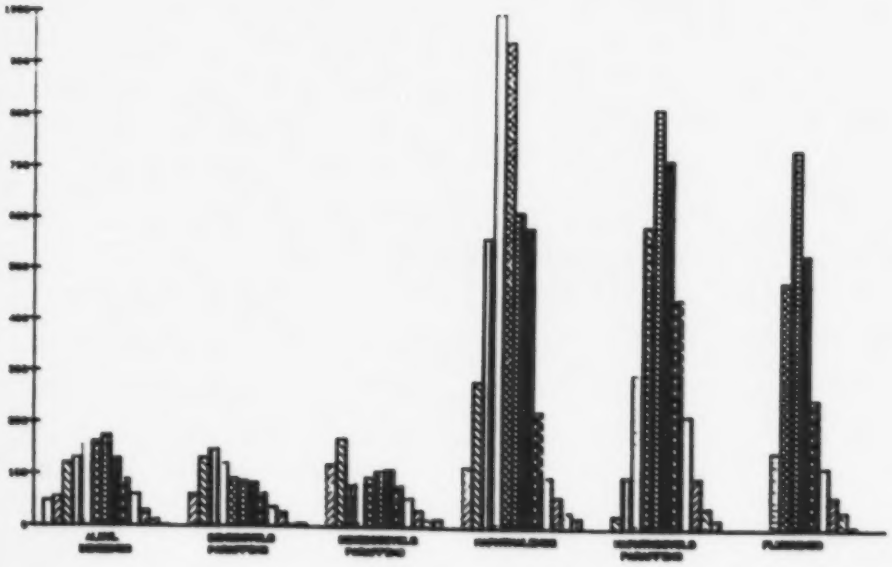
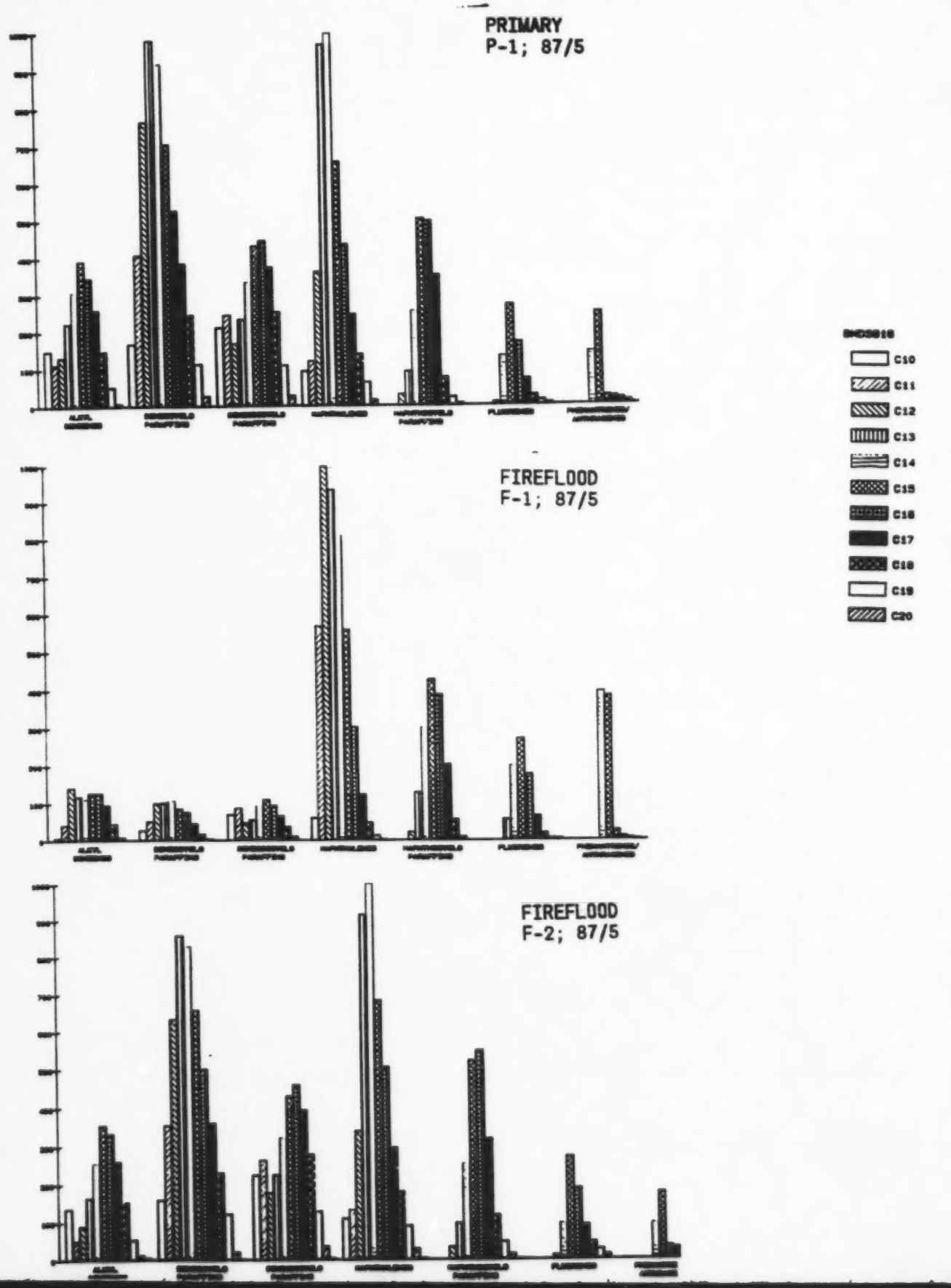
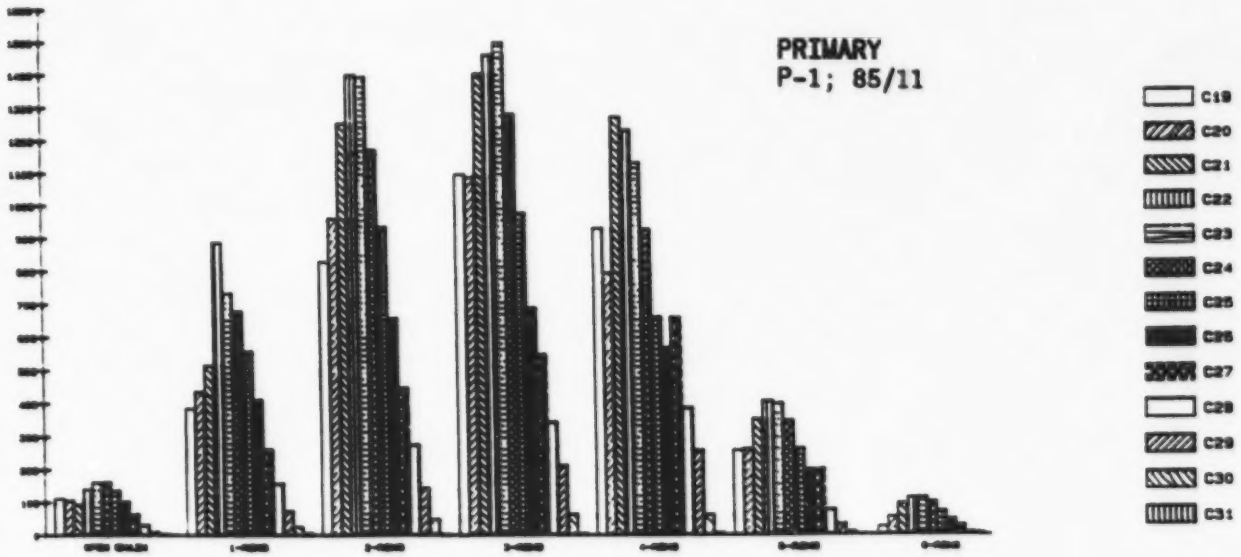


Figure 20(b)

The distribution of compound types in fraction 3 of the middle distillate cut in the 1987 primary and fire flood production samples.



The distribution of compound types in the saturates fraction of the gas oil distillation cut of the 1985 primary and fire flood production samples.



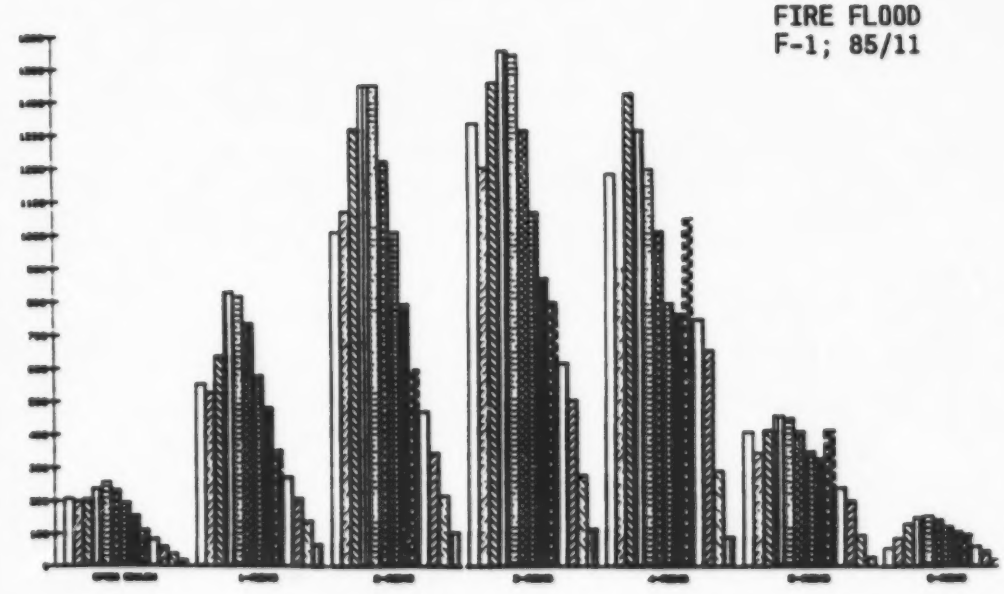
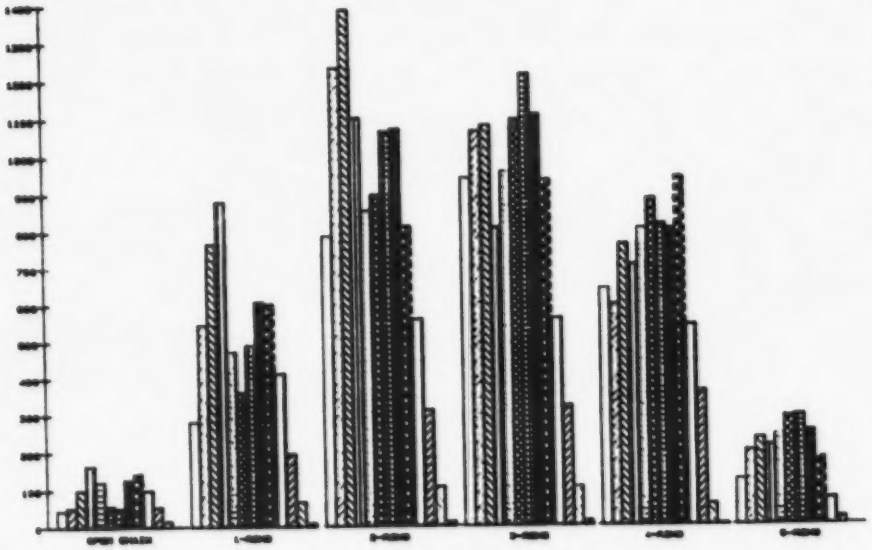
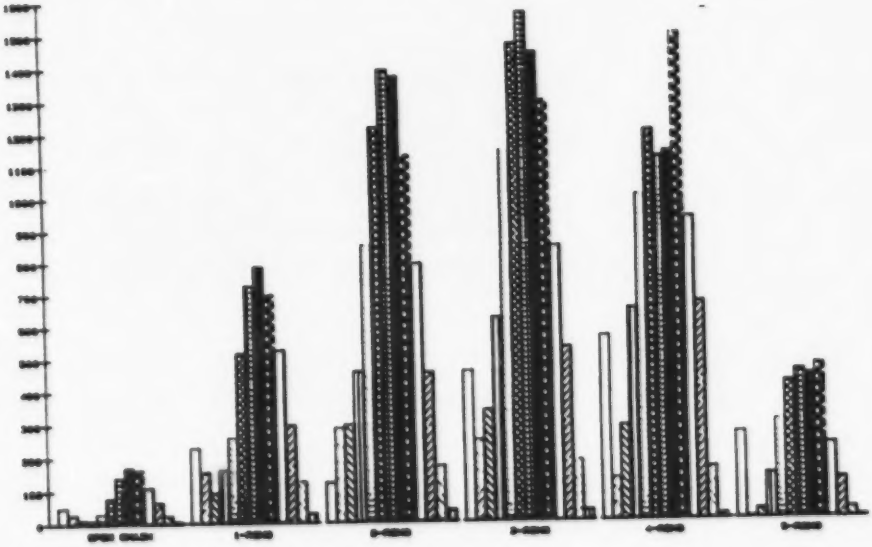


Figure 21(B)

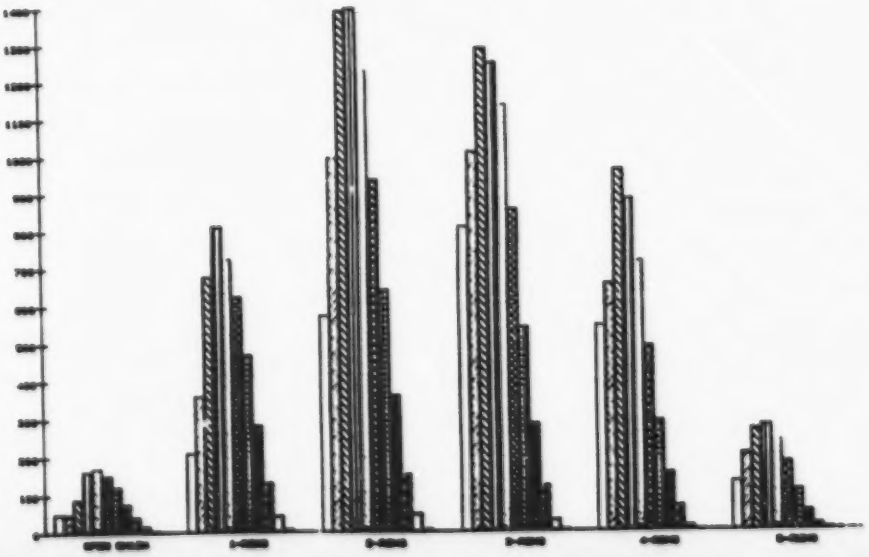
The distribution of compound types in the saturates fraction of the gas oil distillation cut of the 1987 primary and fire flood production samples.



PRIMARY
P-1; 87/5



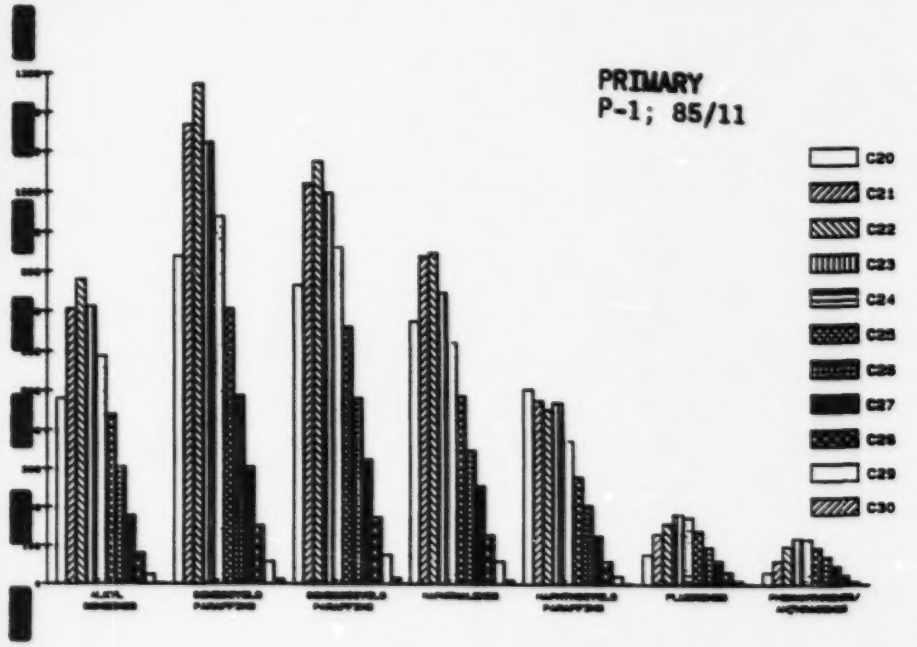
FIREFLOOD
F-1; 87/5



FIREFLOOD
F-2; 87/5

Figure 22(A)

The distribution of compound types in the aromatics fraction of the gas oil distillation cut of the 1985 primary and fire flood production samples.



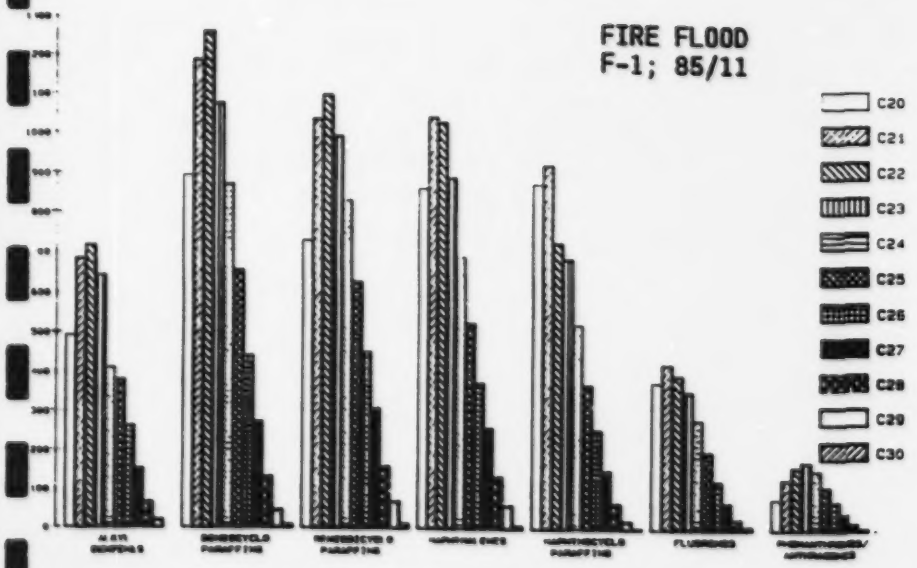


Figure 22(B)

The distribution of compound types in the aromatics fraction of the gas oil distillation cut of the 1987 primary and fire flood production samples.

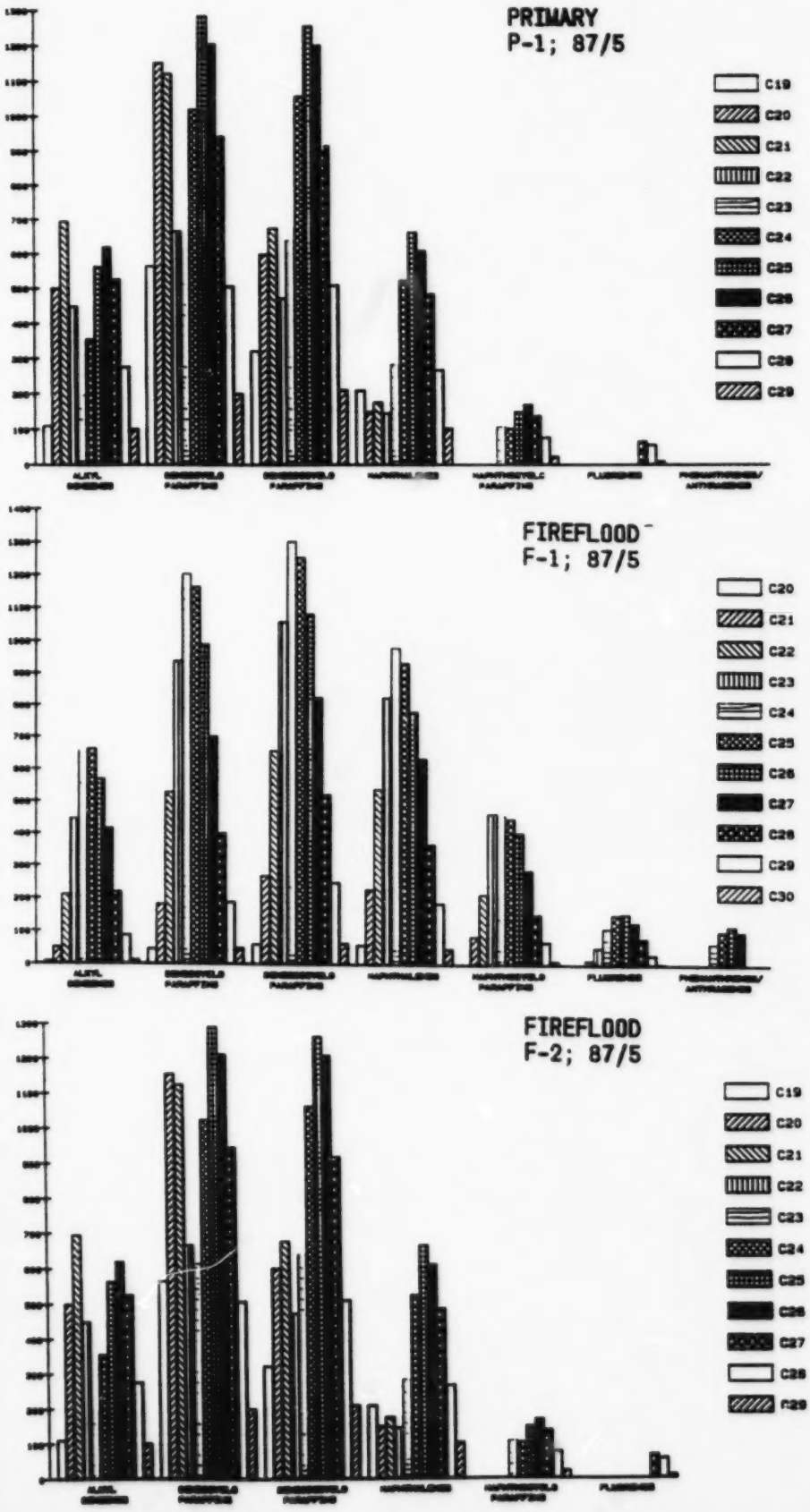


Figure 25(A)

The distribution of compound types in the fraction 3 of the gas oil distillation cut of the 1985 primary and fire flood production samples.

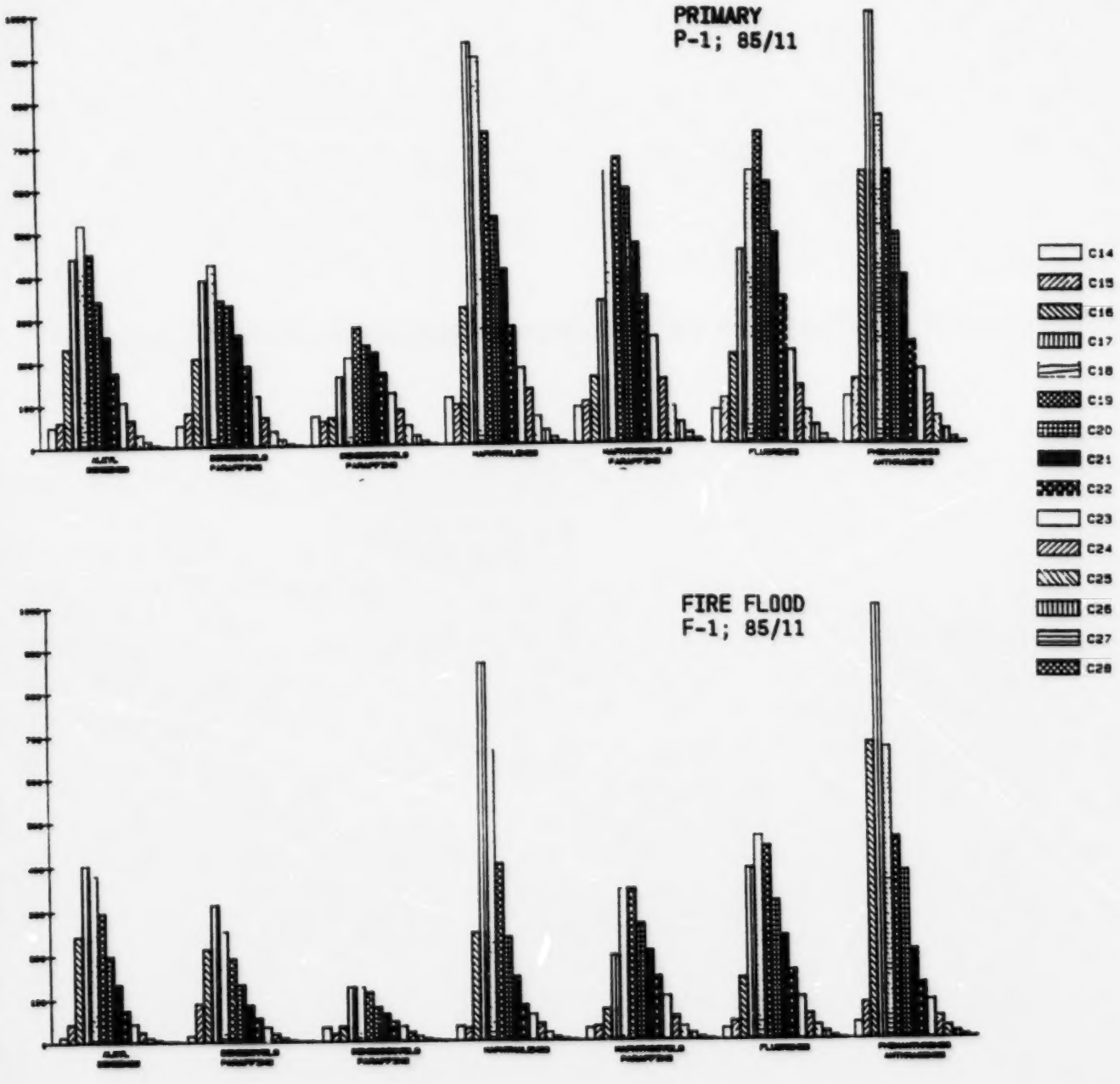


Figure 23(B)

The distribution of compound types in the fraction 3 of the gas oil distillation cut of the 1987 primary and fire flood production samples.

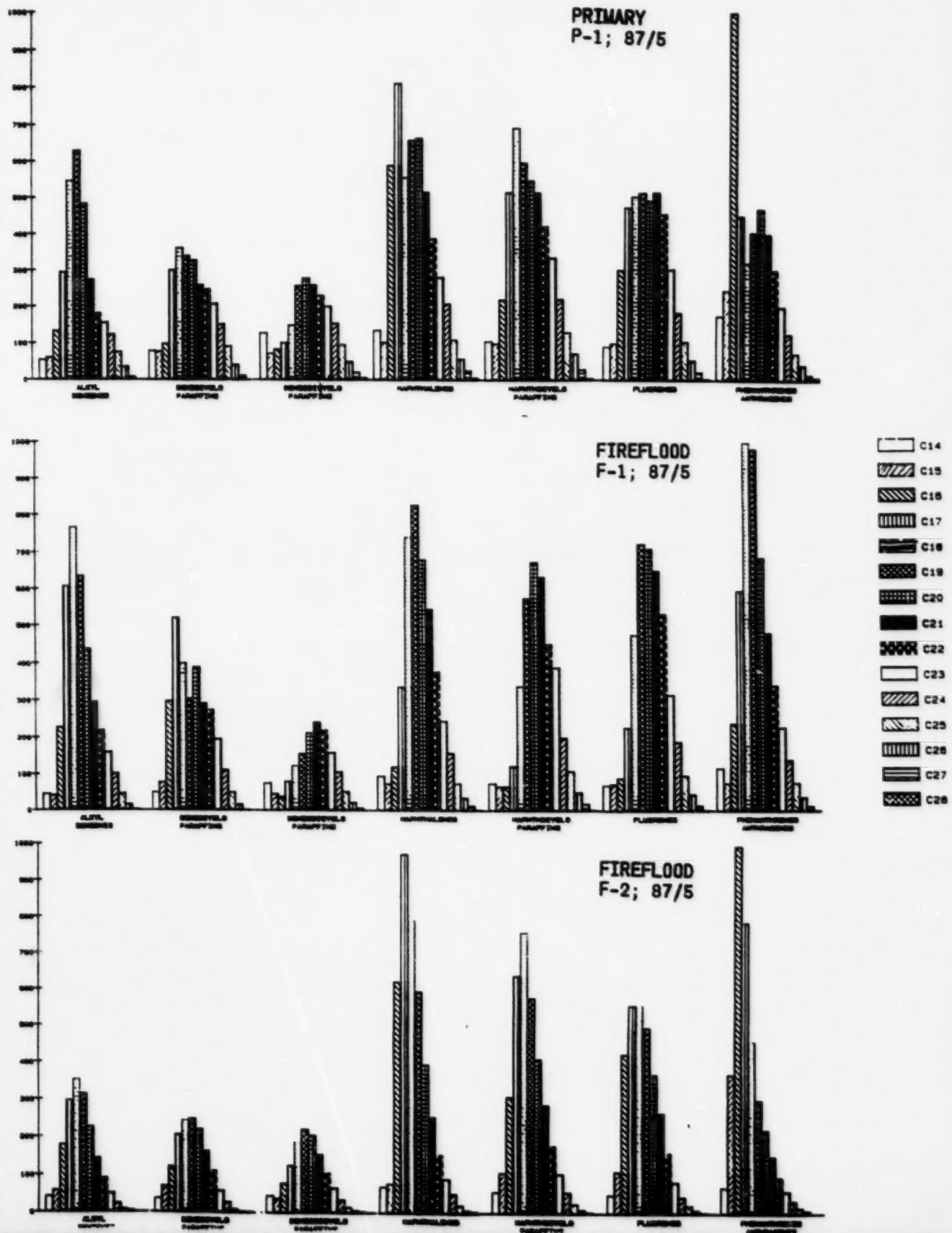


Figure 24

The distribution of compound types in the saturates fraction of the distillation residue of the 1987 primary and fire flood production samples.

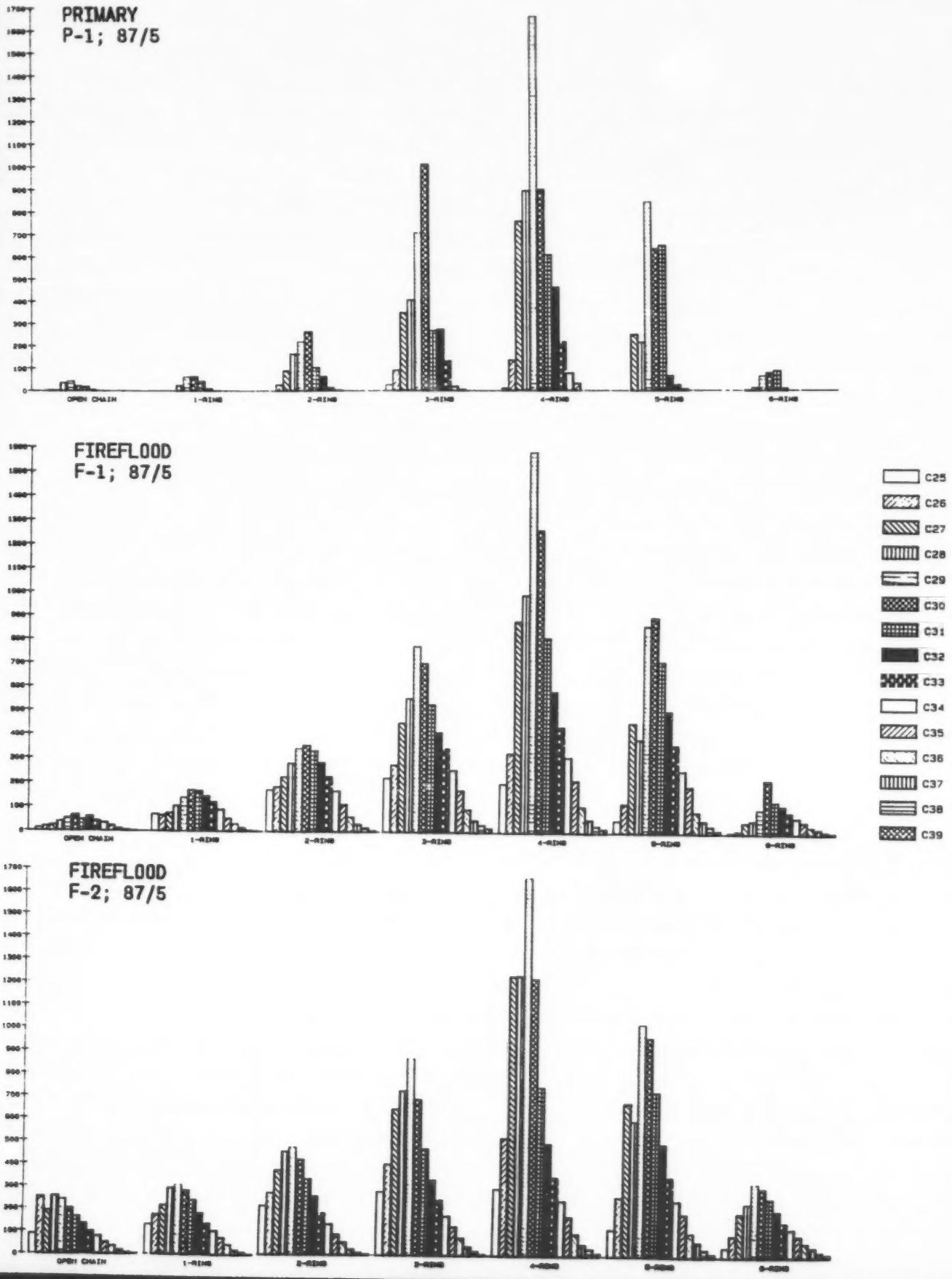


Figure 25.

The distribution of compound types in the aromatics fraction of the distillation residue of the 1987 primary and fire flood production samples.

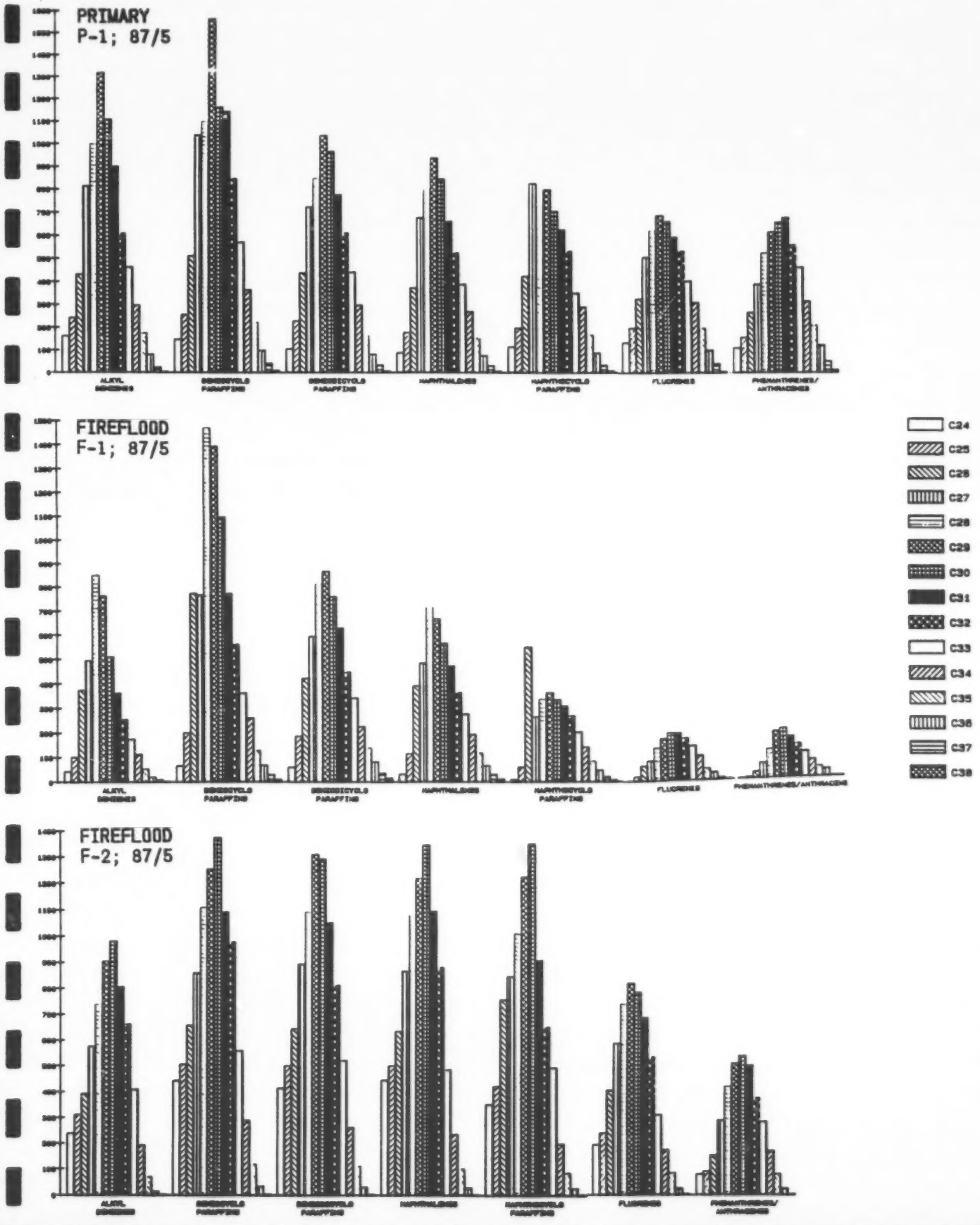


Figure 26

The distribution of compound types in the fraction 3 of the distillation residue of the 1987 primary and fire flood production samples.

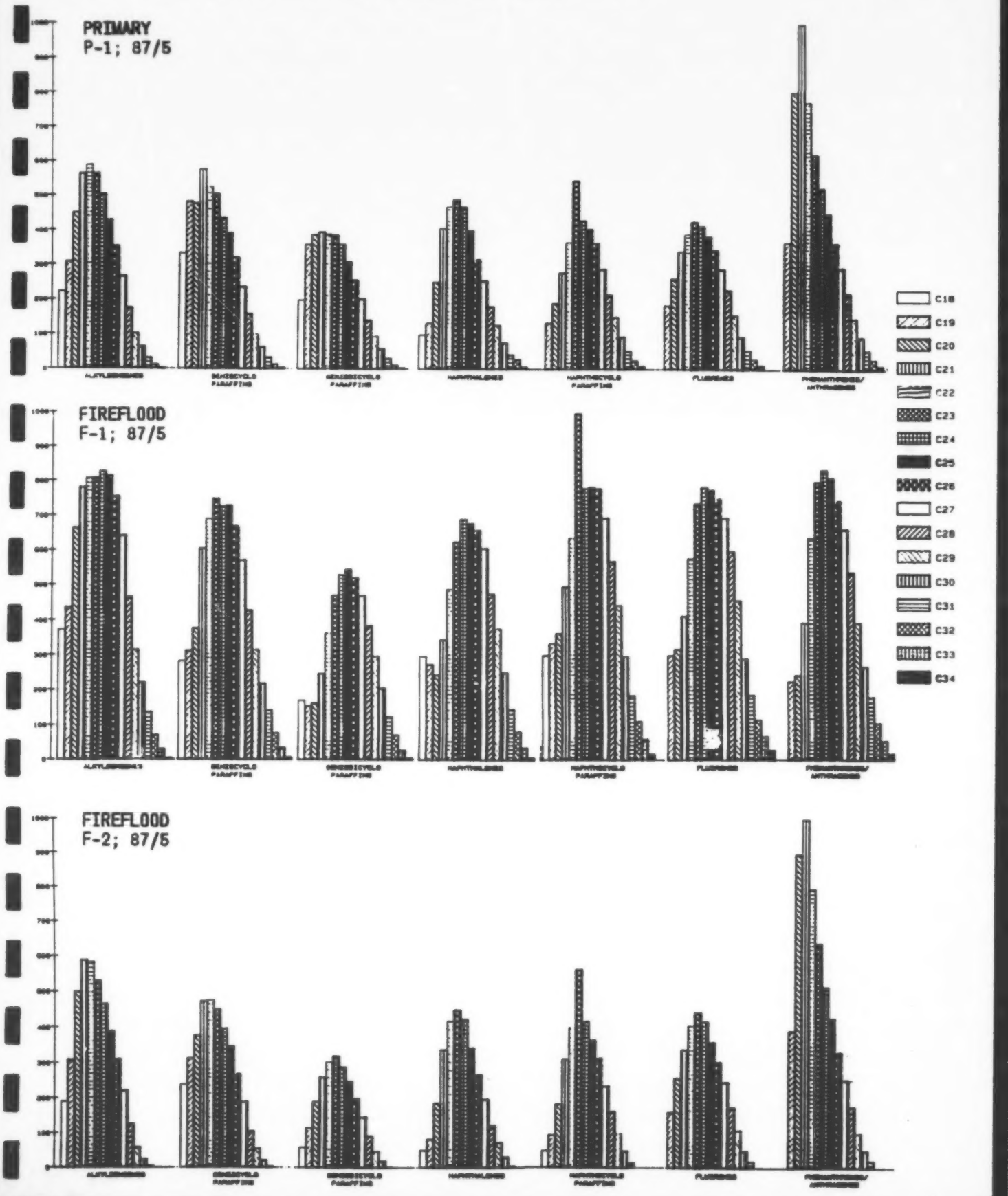


Figure 27

The Gel Permeation Chromatograms of the asphaltenes from the 1985 primary and fire flood production samples.